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CHEMISTRY

In its Relation to the Arts and Manufactures.

— BY —

W. R. LANG, D.S.,

PROFESSOR OF CHEMISTRY
IN THE UNIVERSITY OF TORONTO.

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Canadian Manufacturers' Association

AT THE TEMPLE CAFÉ, TORONTO,
APRIL 25TH, 1901.

CHEMISTRY

In its Relation to the Arts and Manufactures.

In discussing a subject such as you have asked me to bring before you to-night, it is only possible for me to take up the matter in a general way, more with reference to the industries of Canada, and, at the same time, to consider how best these industries may be benefited and developed by the application to them of sound, general and scientific training. Chemistry may be defined as the science which deals with the composition of matter, and, as all industries of whatever nature involve chemical processes of one kind or another, it may safely be said that no industry can succeed without chemistry. It would be impossible, and, indeed, out of place, to discuss any special branch or branches of the arts relating to the many interests at work throughout the Dominion, and represented by the members of this Association. We have purely chemical processes being carried on, the making of acids, alkalies and chemicals in London, Ont.; drugs and soaps at our very doors, and explosives in Hamilton. Besides these, there are iron works, steel works at Hamilton and Midland, cement at Owen Sound, paper, pulp, leather, sugar refining and the production of nickel steel. More

recent articles of trade, such as carbide, for the making of acetylene for illuminating and heating purposes, carborundum and the metal aluminum are being produced comparatively near at hand. All these industries have been dependent on chemistry, and, as knowledge of that science has increased, so in like manner have processes improved, more perfect articles been produced, and the comforts of life—not to mention wealth—been augmented. To the trained chemist, aided by the engineer and the man of business, we are indebted for this, and on looking back into the lives of many of this world's greatest chemists—famous in the domain of theoretical chemistry—we find that most of them devoted a no inconsiderable amount of their time and energies to eminently practical points relating to the arts and manufactures. John Dalton, of Manchester, whose atomic theory is, so to speak, the creed of the modern chemist, interested himself in the industries of his native city. To him came the manufacturer and the dyer for information, and he was the universal referee in all matters pertaining to the purity of water and the genuineness of drugs. Playfair, of Edinburgh; Liebig; Hofmann; Thomas Anderson, of Glasgow, whose work on the pyridine bases is classic, all assisted in developing the industrial side of the science, while, on the other hand, we find men who were engaged in technical chemistry contributing to the literature of the times papers on purely theoretical deduction from phenomena observed during the progress of their ordinary avocation. One of the latter

—a chemical manufacturer—not only wrote a text book on chemistry, which may be found on the shelves of most university libraries, but contributed an excellent article to a contemporary entitled "On the Advantages of Literature and Philosophy in General, and Especially on the Consistency of Literary and Philosophical with Commercial Pursuits." Looking as far back as 100 years, we find the chemist solving problems of vast industrial and national importance. During the Napoleonic wars, the supply of alkali for the manufacture of soap was cut off as a consequence of hostilities with Spain, from which country it had been almost exclusively imported in the form of "barilla." The prospect of a soap famine was too much even for our Gallic brethren, and a valuable prize was offered by Napoleon for the best method of converting common salt into soda. This reward was gained by Leblanc, and to this day the process bearing his name is in use all over the world. There, the art of the chemist played its part; in the first operation for the conversion of common salt, large quantities of hydrochloric acid were evolved and allowed to escape into the air to the detriment of vegetation and health. This in later years was collected by absorption in large towers filled with coke, over which water was allowed to trickle, and from the acid thus saved is now manufactured bleaching powder and other substances indispensible to the arts. Among the former waste products might be mentioned "soda waste," produced during the Leblanc process, and

which for years was neglected as useless. Now the chemist, by a simple and cheap process, in which atmospheric air and the waste acid before referred to play the principal part, obtains from it quantities of sulphur previously looked upon as irreclaimable. Again, we find that furnace gases can be utilized instead of being dissipated into the air, and the production of useful chemicals in this manner bears favorable comparison with the output of the main product aimed at.

Briefly, then, let us consider for a few moments some of the advances that chemistry has assisted to bring about in the direction of producing new commercial articles and utilizing available material. The iron and steel industries in Ontario bid fair to be reckoned soon among the largest in the world ; the pulp output, too, is enormous, and the supply of raw material almost inexhaustible. The chief natural source of the world's nickel supply is in Canada, at Sudbury, where huge quantities of *pyrrhotite* are found ; when nickel oxide or crude nickel is added to iron or steel, the resulting alloy is remarkable for its strength and elasticity, and is preferred before all others for the construction of armour plates, guns and other weapons. The actual methods of separating nickel from its ores and from the other metals associated with it present many difficulties, but, without doubt, in the course of time, the chemist and metallurgist will be able to reduce the cost of production considerably. In practically all metallurgical processes fuel is essential, both as a source of heat and as a

reducing agent, and a case in point occurs to me in which the directors of a company I know of, by not making sure of a convenient source of fuel, brought the undertaking into the hands of the liquidators.

The possibility of producing our own sugar supply from beets is at present looming large in the public eye. Given a proper supply of home-grown beets, there is no reason why the industry should not, in time, become a very large one. The chemistry of the sugars has now reached a high state of perfection, and much is known regarding the different kinds of sugars. Nevertheless, it is open to question whether cane and beet sugar are absolutely identical. One drawback to the latter kind is met with in the mother liquor or molasses ; it cannot be used for human consumption, owing to the small quantity of some poisonous substance or substances that it contains. The molasses from cane sugar, on the other hand, is familiar to all. Probably chemistry will find means to utilize the former variety for other purposes than at present. The crushed beets, after extraction, though containing only a small amount of sugar, could be utilized as fodder.

Of recent years, three new industries have sprung up close at hand which deserve mention as being the outcome of research in the domain of experimental chemistry. I refer to the production of carborundum, calcium carbide and aluminum by means of the electric furnace, for the working of which the falls at Niagara have been partially harnessed. The experiments which led to the discovery of carborundum were

made in 1891 by Mr. E. G. Acheson, who, like many other chemists, hoped to obtain carbon in a crystalline form. Clay and carbon were subjected to the temperature of the electric arc in an iron vessel lined with carbon. It was hoped that the aluminum produced by the reduction of the clay might dissolve some of the carbon, which would again separate out on cooling. Crystals of a very hard material were obtained, brittle and capable of scratching diamond. Further investigation showed that the new substance contained carbon and silicon only, discounting small traces of alumina, iron oxide, lime and magnesia, amounting in all to about 1 per cent. The use of clay in its manufacture was, therefore, stopped, and sand substituted. The new material has found many uses, principally as an abrasive, in the form of hones, as a substitute for emery paper, for polishing plate glass and hides. It is superior to emery, and it is claimed that carborundum can do twice the work of the same amount of emery, and with better results. Though only a child of nine years of age at present, it has already taken its place among chemical industries. During the first six years of its existence, the output rose from 15,000 lb. to nearly 800,000 lb., while the price of $10 per lb. became reduced in the same period to 15c. Calcium carbide, too, as a commercial product, was first obtained during the preparation of aluminum, and immense quantities of it are now manufactured, both at Niagara and in Scotland, for the preparation of acetylene gas, so much used at the present time as an illuminant.

Let us now consider how best chemistry may be applied for the improvement and development of our national industries. Where new substances are to be produced or methods modified to meet the ever-increasing competition approaching from all sides, it is necessary that experiments be tried in the laboratory, and thereafter that plant be designed and constructed for the proper, and economical carrying out of the work on the commercial scale. Here the services of the engineer and mechanic must supplement the knowledge of the chemist. It by no means follows that a process successful on the small scale will be equally so when carried out under trade conditions; the time taken to work out such practical problems is always great. Professor Barr, of Glasgow University, whose range-finder is now to be found on almost every battleship in the navies of Britain, the United States, Japan, and, I think, Germany also, informed me once that the principles on which this ingenious instrument is constructed were evolved in a few weeks, but the practical details of the manufacture required eight years of constant work before success crowned his efforts. The principles underlying the making of carbonate of soda by the Solvay process are known to all students of chemistry, but its practical working on the commercial scale required all the energies of such men as Bond and Solvay himself to be devoted to it before the industry became established on a sound footing. The matter of the proper training of men capable of taking an active part in the development of industries involving chemi-

cal processes in any way has for two years past occupied the close attention of the practical men in Great Britain. The eminent research chemist, Dr. W. H. Perkin, has expressed himself strongly on the need of drawing together the chemist and the constructor, and Mr. Geo. Beilby, the former President of the Society of Chemical Industry, has brought the subject under the notice of the most influential section of chemical manufacturers. One hears reiterated every day that "No good can come out of Nazareth," that is to say, that chemical manufactures are a dead letter in British dominions, and that in Germany only is the true home of industrial chemistry. In a measure this is true, but one has only to visit the large manufacturing towns in Britain to see that chemical industry is by no means dead, but, on the contrary, flourishing "like the green bay tree." Where are bichromate of potash and alum produced most cheaply? In London and in Glasgow. Where are the most extensive sugar refineries, leather works, soap works, iron and steel works? In the smoky towns of the Mother Country. Where are refined chemicals produced more cheaply than anywhere else, laboratory glassware and toys? In Germany. Where is pulp produced, iron, steel, nickel and agricultural implements? In Ontario. Each country has its own staple products, and the outcry regarding the decadence of our Imperial industries appears to me to be overdone. But this very outcry should be a warning and a safeguard; we must, so to speak, "to prevent war be prepared for war," and to be

prepared for the industrial war—not a mere guerrilla one either—which will surely come upon us from all sides, we must prepare ourselves and endeavour to improve our present resources to the utmost and agree as to the best means of doing so. I should like to quote from an address given three years ago by Dr. Edward Schunk, F.R.S., at the annual meeting of the Society of Chemical Industry:

"A great deal has been said of late as regards the dangers of our manufacturers from competition on the part of foreign producers. * * * From the speeches which are now and then made, one would infer that the danger is real and imminent, and that it behoves us with all possible speed to build and endow technical schools in which our workmen and others shall be trained so as to enable them to compete with the more highly educated classes of similar standing in Germany and France. I am myself too little in touch with the manufacturing industries of the present day to say whether the danger is real and present or merely apprehended and distant. If, however, it be permitted to draw conclusions from what one sees in travelling on the Continent, one might infer that competition with this country in many articles of trade is, at present at least, quite chimerical. Who that has seen what is offered to us in France and Germany in the shape of furniture, glass or china, can help thinking that were free trade established between these countries and ours, many of the poor, inferior articles of their commerce would be swept away to give place to really

good substantial ones such as we could furnish, or which they could themselves produce if exposed to the healthy influence of competition. In some departments of industry, especially the chemical, and more especially that of colouring matters, foreign competition is, I suppose, a very serious matter, but whether the evil is one that can be remedied by mechanical and educational measures seems to me doubtful. The fact is, that successful foreign competition may be due not only to superiority of education and training, but also to certain inscrutable, perhaps moral qualities, of which it is difficult to estimate the weight and bearing. As long as human beings exist there will always be differences of talent and disposition between individual and individual, and between one nation and another. In technical, as in other matters, special talents show themselves. The English have always been known for great mechanical undertakings, the Germans and French for the manufacture of chemicals, especially those of organic nature. That specialities such as we see developed on a large scale in the case of different nations are also seen on a smaller, in our own and other countries, is well known to everyone. Boots and shoes are made in one place, hats in another. The woollen trade flourishes in Yorkshire, and different branches of it in different towns. In this country, likewise, different branches of the cotton trade have localized themselves in various places. Why we should deplore this state of things I am at a loss to understand. Why should we not buy what we want where we can buy it

best and cheapest? Why should we determine to make all we require ourselves? These questions have often been asked and been answered by us in this country in one sense, and in other countries in a contrary sense."

If we wish to succeed, then, in the proper exploitation of our natural resources, we must employ properly-trained men for that purpose. In my inaugural address in the University some months ago, some extracts from which your Executive deemed of sufficient interest to this Association to merit publication in the Society's journal, I expressed myself in effect that the thoroughly-trained university man was the man to be looked to to help in this object. The true secret of successful manufacture consists in the close collaboration between the research chemist and the works manager. The usefulness of scientific training is now more than ever being demonstrated, and daily we see that the chemical industry which arises from the classroom and the laboratory is surely vindicating its superiority over the rule-of-thumb methods employed by the works foreman. To refer only to places of business with which I am familiar, a complete cycle—indeed, an overlapping of the circle—has been traversed in respect to the staffing of factories. Twenty and twenty-five years ago, trained chemists in the Old Country found lucrative positions in establishments large and small, but, as years progressed, the shortsightedness of employers to the adage that "the highest salaries yield the cheapest work" led their places to be filled by raw youths, whose

only pretention to chemical knowledge was their having spent from six months to two years in some analytical laboratory without any systematic training in general scientific subjects—in short, with utterly untrained minds on even general subjects. Such men, the employers found, could be got for a salary of from $400 to $500; they could be trained to do laboratory work in a machine-like way, and which, for the time, satisfied their business chiefs. The results of this might easily have been prophesied; either the youth became a mere drudge, or, if he displayed any originality and took an interest in his work sufficient to let him summon up courage to ask for a rise in salary, his place was most probably promptly filled by another at the same magnificent rate of pay. Foreign competition and advances in chemical knowledge soon demonstrated the shortsightedness of this policy, and now, I happy to say, places *can* be got by men with a thoroughly-sound academic training in science generally, which carry with them a reasonable salary and offer an unlimited field for the man with application and ability to further his own and his employer's interests.

And yet another matter which the manufacturer would do well to consider: In what manner does he intend to bring to the notice of his customers the goods he has to offer? I maintain that it is not sufficient for him to send out commercial travellers to push the sale of his products whose whole qualifications are that of being good salesmen; the manufacturer must come into personal contact with his customers, or employ

men to do so who are capable of directing them, understanding their desires, teaching them how best to employ their purchases and indicating which particular article is most suited to their wants. An eminent and successful electrical engineer in my own city — a brother of my colleague, Professor Mavor—told me that this method had been adopted by our cousins in the United States, and that the agents employed by all firms of any importance were men of sound education and intelligence, possessing a thorough grasp of all the details of the industry they represented. The natural consequence is the establishment of mutual collaboration between themselves and the customers whom they advise, and the customer, in turn, reciprocates the evident interest taken in his wants by consulting with the seller as to how he can best have his requirements met.

I would now like to bring before you, and particulary before those of my hearers whose business may from time to time present problems they find difficult to solve satisfactorily, the following suggestion contained in an address to the Society of Chemical Industry delivered by my friend, Mr. Beilby:

"This subject of Industrial Problems and Researches may be cleared of some difficulty if we begin by recognizing that industrial problems may be divided into two perfectly distinct classes. There are the problems the mere statement of which by a manufacturer would give his rivals a dangerous amount of insight into his operations and methods. No one who has the ability to evolve such

problems would be foolish enough to give his position away by publishing them.

"But, there is another class of problems, the publication of which will do good and not harm to the manufacturer. Where an industry is encumbered with some waste produce which is common to all of its manufacturers, all of whom are practically on a common level in its disposal, there is clearly room for the importation of skill and originality from outside of the industry. There are, further, those cases in which a considerable amount of research is required before the thing desired by the manufacturer can be even stated as a problem. There are many branches of industry which are practically without scientific experts who could initiate and carry on research. In such cases it appears to me quite worth while to try to educate the manufacturer to appreciate the value of pure knowledge, even if it does not immediately lead to practical results in his works. If we can induce such manufacturers to advertise their wants we shall have begun their education in a very hopeful way, and we trust that the response to their advertisement will be such as will increase their confidence in the value of research. I will only give one illustration, which may make my meaning clearer.

"The Scotch shale oil industry produces annually about 50,000,000 gallons of crude oil. Only about 70 per cent. of this oil is obtained as refined products, 30 per cent. being lost as coke, gas and tar. The tar is composed chiefly of basic nitrogenous substances, which are separated from the oil by

treatment with sulphuric acid. These 'acid tars' are partially washed with water for the recovery of sulphuric acid, and the washed tar is burned under the oil stills as fuel. Its value for this purpose is from 12s. to 18s. per ton. The total production of these tars in Midlothian and Westlothian is about 30,000 tons a year. Numerous attempts have been made to utilize these tars in some more advantageous way, but without success. After sharing in these attempts for many years, I have come to the conclusion that our knowledge of this material has not yet reached the stage at which we can profitably state problems about it. What is required is that it should be thoroughly investigated, so that we may know the pure substances of which it is mainly composed and their constitution and properties. Who will do this? The oil works chemists and their assistants have their time and attention fully occupied with the routine of the manufacture, therefore, they cannot make the research. If the various companies were to combine to establish a research labratory, they would have to place themselves and the problems entirely in the hands of the chemist whom they appointed chief, and who might or might not be capable of bringing their research to a practical issue. Is this not a case in which it is better to invite chemists at large to take up the research? Are the chances of finding the right man for the work not enormously greater in this way than they would be in any other system of selection?"

In order to carry out this idea, then, let me suggest that when difficulties occur

recourse be had to those whose special training and circumstances permit of careful investigation of the subject. Where no secrecy is required and the services of the professional man consequently not called for, why not offer a prize for the satisfactory solution of the problem? At our universities there is always a sprinkling of graduates carrying on original research and who would be glad of the additional financial incentive to exercise their ingenuity and skill in clearing up the difficulty. At the same time they would be benefiting the manufacturer and indirectly the country while improving their own qualifications for an appointment in a sphere of future usefulness.

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ACTION OF POTASSIUM PERMANGANATE ON INDIGO, WITH REFERENCE TO THE DETERMINATION OF NITRATES BY THE INDIGO-CARMINE METHOD.

BY

W. R. LANG, D.Sc., AND W. M. WILKIE.

LONDON:

EYRE AND SPOTTISWOODE, EAST HARDING STREET, E.C.

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ACTION OF POTASSIUM PERMANGANATE ON INDIGO, WITH REFERENCE TO THE DETERMINATION OF NITRATES BY THE INDIGO-CARMINE METHOD.

BY W. R. LANG, D.Sc., AND W. M. WILKIE.

A series of experiments with dilute potassium nitrate, sulphuric acid, and indigo, titrated with N/10 permanganate of potash, gave such anomalous results for the same amounts of potassium nitrate and indigo when the quantities of sulphuric acid and of water varied, that the authors, in this paper, have endeavoured to determine the causes to which the previous failures to obtain any comparable results in the above titrations might be attributed.

The solutions employed were made as follows:—

Indigo.—1 grm. of pure indigotin was treated with 40 c.c. of concentrated sulphuric acid for an hour at a temperature of 70° C. The solution, on cooling, was made up to 1 litre, and of this, 10 c.c. diluted with 100 c.c. of distilled water was employed for each experiment.

Decinormal Potassium Permanganate. — The permanganate was standardised against pure iron wire, the iron solution being reduced in a Jones reductor. For use the solution was made centinormal.

I. *Titration of Indigo Solution by Permanganate in the presence of Sulphuric Acid.*—10 c.c. of indigo, 100 c.c. of

Indigo.	Water.	Sulphuric Acid.	Permanganate required.	
			I.	II.
c.c.	c.c.	c.c.	c.c.	c.c.
10	100	1	24·75	25·7
10	100	2	24·77	27·5
10	100	3	25·00	27·9
10	100	10	25·73	28·0
10	100	25	25·80	28·6
10	100	50	26·18	30·2
10	100	100	31·43	48·8

water, and varying amounts of sulphuric acid were titrated with N/100 permanganate; in the first column are the quantities of permanganate required when no attention was paid to any increase in temperature consequent on the addition of the sulphuric acid, and in the second column are the amounts required when the temperature was kept constant at 100° C. during titration.

From these results, each one obtained from at least four titrations, it is apparent that the amount of sulphuric acid present exerts a considerable influence on the action of the permanganate on the indigo, and also that the temperature at which the reaction takes place is an important factor, the sulphuric acid evidently attacking the permanganate readily, as in the last example, where, it will be noticed, almost double the amount of permanganate is used as in the first. Experiments of a similar nature, but running the permanganate into the solution at different rates, showed that the reaction between it and indigo was a slow one, as much more was required than when the oxidising solution was added slowly. In all the experiments, therefore, the permanganate was added at a definite rate.

II. Adhering to this definite rate of adding the permanganate, further determinations of the permanganate required to decolorise 100 c.c. of dilute indigo (0·1 grm. per litre) in the presence of an equal volume of concentrated sulphuric acid were made, as in the method recommended by Trotman and Peters (this Journal, 1902, 694) and other writers. After mixing the acid and the indigo and bringing the temperature to 100° C., and titrating—occupying 15 minutes in this operation—with the temperature kept as nearly constant as possible, the amounts of permanganate required were 45·15, 46·5, 42·2, and 43·05 c.c.

II.(*a*).—Repeating the above with only 50 c.c. sulphuric acid under precisely similar conditions of temperature, time, and the rate of adding the permanganate, from 30·18 c.c. to 30·2 c.c. were required, the end point being quite accurate and practically constant.

III.—Experiments made with water and sulphuric acid in varying amounts, and permanganate added, gave the results shown in the subjoined table.

IV.—Lastly, the effect of a dilute solution of a nitrate (1 grm. KNO_3 per litre) on indigo in the presence of sulphuric acid was tried; the end point was difficult to deter-

Water.	Sulphuric Acid.	N/100 Permanganate required to produce any colouration.
c.c.	c.c.	c.c.
100	1	0·25
100	2	0·25
100	5	0·35
100	10	0·45
100	50	1·25
100	100	(from 6 c.c. to 8 c.c., depending on the rate of adding the permanganate.)

mine, but the following figures will show how much depends on keeping the temperature constant, and for the same length of time :—

KNO_3 Solution.	Water.	Sulphuric Acid.	Time of heating at 100° C.	Indigo required.
c.c.	c.c.	c.c.	Mins.	c.c.
10	20	10	5	15·8
10	20	10	10	17·9
10	20	10	15	17·3
10	20	10	15	7·5
10	20	10	15	2·0

In the last three experiments (15 minutes' heating) the temperature was allowed to rise in each case further above 100° C., the results thus obtained being due to loss of nitric acid.

If, then, this method of estimating nitrates is to be of any accuracy, an *absolute similarity of conditions, both as regards time and temperature, must be observed.* It would appear from the results quoted in II.(*a*) that half the volume of concentrated acid would act better than a solution containing equal volumes alike of water and indigo and of acid. The figures given here may, it is hoped, help to explain certain anomalous results obtained and difficulties met with by users of the indigo-carmine method.

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THE CHEMICAL INDUSTRIES OF CANADA.

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Canadian Section.

Meeting held at Toronto, on Wednesday, May 6th, 1903.

DR. HAROLD VAN DER LINDE (VICE-CHAIRMAN) IN THE CHAIR.

CHAIRMAN'S ADDRESS.

THE CHEMICAL INDUSTRIES OF CANADA.

BY W. R. LANG, D.Sc.

In selecting a subject for an address as the first Chairman of the Canadian Section of this Society, two main considerations have been kept in mind; firstly, that the development of the industrial resources of the Dominion during the past decade has been phenomenal, and, secondly, that the extent of these developments is only fully understood by a few, while it is almost unknown to our fellow members in Britain. While it is impossible to discuss *all* the industries in which chemical operations and reactions are made use of, an attempt has been made to select processes in some cases peculiar to the country, but notably the industries which owe their development to the natural, mineral, and vegetable resources, and to the widely scattered water power obtainable in the Dominion.

The subjects taken up may be classified as follows:—

I.—Common Salt, Alkali, and Chlorine Compounds.
II.—The Extraction and Refining of Metals.
III.—The Leather and Tanning Industries.
IV.—Sulphuric Acid, Acetic Acid, Wood Alcohol, Charcoal, and Ammonia.
V.—Soap and Glycerin.
VI.—Refined Chemicals and Drugs.
VII.—Fertilisers.

VIII.—Coal-Tar and Asphalt.
IX.—Calcium Carbide, Carborundum, and Graphite.
X.—The Cement and Plaster Industry.
XI.—Carbohydrates: Divided into—
(*a*) The Refining of Sugar.
(*b*) The Beet-Sugar Industry.
XII.—Natural Gas and Petroleum.
XIII.—Pulp and Paper.
XIV.—Asbestos.

I.—Common Salt, Alkali, and Chlorine Compounds.

Sodium chloride is found in the Upper Silurian beds in Ontario and in the Devonian in Manitoba and Athabasca; salt springs also occur in Cape Breton and in New Brunswick, but these are comparatively unimportant sources of supply. In Ontario the salt area stretches through the counties of Middlesex, Huron, Bruce, and Lambton, large deposits being found along the shore of Lake Huron from Kincardine to Windsor. At Coderich there is a deposit 126 ft. thick, and at Windsor a well extending to a depth of 1,672 feet passes through four beds of rock salt of an aggregate thickness of 392 ft.[1] The salt is obtained by evaporation, and is of an excellent quality. The following comparison serves to illustrate the purity of the natural product.[2]

	Natural Salt of Coderich, Ontario.	Natural Salt of Cheshire (England).
	Per Cent.	Per Cent.
Sodium chloride	99·687	96·70
Calcium chloride	0·032	0·68
Magnesium chloride	0·095	0·00
Calcium sulphate	0·090	0·25
Moisture	0·079	0·63
Insoluble matter	0·017	1·74
	100·000	100·000
Total impurities	0·234	2·67

[1] W. Hodgson Ellis, M.B., in "A Handbook of Canada," 1897.
[2] Wilmott, A. B., "Some Minor Minerals of Canada," 1897.

The total production of salt in Canada was valued in 1892 at 162,000 dols., and in 1901 at 262,328 dols.

Apart from its uses as a seasoning and as a preservative, common salt is employed in the electrolytic preparation of caustic soda and bleaching compounds. (A full description of this industry was given in a paper read before the Society in Toronto by Mr. B. E. F. Rhodin in 1902. See this Journal, 1902, 449).

The alkali and bleaching powder industries throughout the world are at the present time in an unsettled condition, mainly owing to the advent of electrolytic methods.[3] Wherever cheap water power is available, however, electrolytic processes will be rapidly developed.

II.—The Extraction and Refining of Metals.

Almost every province in the Dominion possesses valuable mineral resources; these are rapidly being exploited, and among the metals produced in quantity may be mentioned iron, copper, lead and silver, nickel, arsenic, antimony, and, lastly, aluminium. These metals are found in the form of native iron, magnetic iron ore, iron pyrites, hæmatite, native copper, chalcopyrite, galena, native silver, and ores of silver, nickeliferous pyrrhotite, gold, sulphide of antimony, and arsenical pyrites.

Iron.—The iron ores of the Dominion occur at varied intervals, from Vancouver Island, on the west, to Cape Breton Island and Newfoundland on the east. In Nova Scotia there are particularly rich deposits, and in close contiguity to them are found the necessary materials for smelting. Hæmatites, too, are found in all parts of Canada. One of the most valuable deposits of specular iron is at Hull, near Ottawa, which assays from 64 to 68 per cent. of metallic iron. In the Appendix (Appendix I.) will be found more particulars regarding the iron ores of the Dominion.

The Canadian iron industry dates back to the establishment of the St. Maurice forges by the French Government in 1737. Many other minor plants were subsequently built, as at Batiscan, Hull, and Bois St. Paul, all in Quebec; at Furnace Falls, Mormondale, Marmora, &c., in Ontario; at Woodstock, in New Brunswick; and at Moose River, Nictaux, and Bloomfield, in Nova Scotia. They all

[3] Chem. Tr. J., 23.8.02, 6.9.02, and 24.1.03.

subsequently failed, however, in consequence of the competition of Great Britain and the United States. This early failure was due as much as anything else to lack of enterprise, capital, and proper shipping facilities. The modern development of the industry may be said to date from the introduction of a protective duty on iron in 1887. The granting of bounties by the Dominion and Ontario Governments has also assisted largely in bringing about the present condition of the iron and steel industries.[4] The annual aggregate capacity of the completed and unfinished furnaces in the Dominion in 1901 was close on 1,000,000 gross tons.[5] Much of the iron produced is now being made into steel[6] by the Bessemer process. At Sault Ste. Marie an extensive plant has recently been completed, with a capacity of 200,000 tons of ingots and 180,000 tons of finished products. There, steel rails are being made for the first time on Canadian soil. At Collingwood, Ontario, the Cramp Steel Co. expect to have an output from their new works of from 100 to 120 tons per day, finished into small-size material suitable for blacksmith's and machinist's use. The works of this Company, which are not yet completed, consist of a 250-ton blast-furnace—to be finished this season—and two 20-ton open-hearth steel-furnaces, beside rolling mills. In these furnaces will be utilised equal amounts of pig and scrap iron; the furnaces are lined with magnesite, and the Gilchrist-Thomas basic process will be employed. The machinery for the plant is actuated by electric and hydraulic power, while the cranes are hydraulic entirely. It is claimed that the rolling mills will be the finest in the country.[7] On the eastern seaboard of the Dominion are situated the works of the Dominion Iron and Steel Co., begun in 1899. This company has a capital of 20,000,000 dols. common stock, besides 5,000,000 dols. 7 per cent. preferred stock and 8,000,000 dols. in 5 per cent. bonds. An arrangement has also been entered into with the

[4] Dominion bounty on pig iron, 3 dols. per ton produced. Ontario bounty, 1 dol. per ton on pig produced from Ontario ores, and 50 cents on ores not obtained in the province; the rate of 1 dol. to be only paid up to 25,000 tons. Bounty is at present largely reduced, owing to increased production.

[5] Statistical Year Book of Canada, 1901, p. 160.

[6] Dominion bounty on steel, 3 do's. per ton; 2 dols. per ton on steel from foreign ores.

[7] Letter from Mr. J. A. Currie.

Dominion Coal Co. for a 99 years' lease, paying for the privilege 6 per cent. on 20,000,000 dols. common stock of the latter company. Coal and limestone are found comparatively near at hand, the farthest afield mine from which the coal supply is drawn being 25 miles distant, while the nearest one is 6 miles. There is no lack of this mineral, the output being now from 3 to 3½ million tons per annum, as compared with 800,000 tons in 1898. Nearly all the iron ore at present used is brought from mines owned by company on Great Belle Island, in Conception Bay, Newfoundland, some 400 miles from Sydney. This mine is estimated to contain 28 million tons of available ore, besides areas under the sea, which are believed to be very extensive. Analyses of the ore show it to contain 50 per cent. of iron, little sulphur, but rather too much silica, aluminium, and phosphorus. The result is a pig iron too high in phosphorus, but during the subsequent conversion of the pig into steel in open-hearth furnaces, this impurity is eliminated, and a fine quality of steel produced. For the best kind of pig iron, it is necessary to mix other ores with it, and for this purpose Cuban, Spanish, and Swedish ores are used, the result being a low phosphorus pig. Indications of large deposits of high-grade ores have been found both in Nova Scotia and Cape Breton, which, when fully developed, will in a great measure replace the foreign ores.

Limestone is obtained from the company's quarries at the Bras d'Or Lakes, about 85 miles, by water, from the works. It is a stone of good quality, and is found in large deposits; it acts well with the Newfoundland ore and the Cape Breton coke.[8] The works contain four blast-furnaces capable of yielding 1,000 tons of pig iron per day; the furnace gases are utilised also to the utmost, being used to heat the blast and also to raise steam. The iron produced is partly cast into pigs and in part conveyed in a molten condition direct to the open-hearth furnaces, where it is converted into steel. Of these there are 10 in number, of the H. H. Campbell type of tilting basic open-hearth furnaces, having a capacity of 50 tons each. A very complete arrangement of testing the steel at intervals is in vogue, and of stamping each ingot with special marks so that the consumer can ascertain from the company at any time every particular regarding the analysis and making of the piece.

[8] The daily shipment is 1,500 tons.

The gases produced in the coke ovens are used in the open-hearth furnaces, the other bye-products, namely coal-tar and ammonia, being also collected. The ammonia is converted into ammonium sulphate by neutralising it with sulphuric acid—which can be obtained from the pyrites separated from the coal in the preliminary grinding and washing processes to which it is subjected—and is principally exported to the United States, the West Indies, and Glasgow. The coal-tar at present finds a market in the States, at Montreal, and other points in Canada. Recently arrangements have been made with an English chemical company to locate at Sydney. The works are now in process of construction, and all the coal-tar produced will be utilised for the manufacture of the numerous products of distillation.

Canadian-made steel is largely exported to the United States, whence it returns to Canada in the form of rails and other finished products; but it is intended that this feature of the steel industry will shortly be transferred to Canadian territory. Sydney is extremely well situated as a seaport, being nearer to England than is New York, and, strange as it may appear, to the ports of South America and South Africa.[9] As far as geographical position is concerned, therefore, Sydney possesses many advantages, while the masterly and liberal way in which the iron and steel industry has been organised and developed points to a bright future for it in Canada.[10]

A new plant is being erected near North Sydney by the Nova Scotia Steel Co., who have at present works at Ferrona,

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[9] Sydney Harbour to Liverpool (*viâ* South of Ireland). Miles. 2,307
New York Harbour to Liverpool 3,110
Sydney Harbour to Pernambuco 3,567
New York Harbour to Pernambuco 3,696
Sydney Harbour to Cape Town 6,467
New York Harbour to Cape Town 6,787

These figures were supplied to me by Mr. Watson Griffin, who obtained them from Captain W. H. Smith, R.N.R., Halifax. The distances from New York were compiled by the United States Commission of Navigation.

[10] Mr. Watson Griffin, who kindly supplied me with material from which the above description of the Sydney operations was written, mentioned also that a leading Scottish iron and steel magnate told him that, everything considered, Sydney, in regard to raw materials, nearness to the market, and the excellent equipment it possessed, would be the finest steel manufactory in the world. Watson Griffin, "Dominion Steel and Coal Co., Sydney;" Montreal, 1902. Watson Griffin, "The Front Door of Canada;" Montreal, 1899.

with a limited supply of ore near at hand. Hence they import largely from Newfoundland. Their steel works are at present at New Glasgow, but a new plant is under construction at Sydney. Their output, which is sold almost exclusively in Canada, approximates 100 tons of pig-iron per day, and the same amount of steel. The Canadian Iron Furnace Co., of Montreal, has recently acquired the iron deposits formerly belonging to the Londonderry Iron Co., and is reconstructing the works on the most modern plans.

Copper.—The production of refined copper can hardly be classed among the chemical industries of the Dominion, as practically only the first stage in the extraction of the metal is reached, namely, the making of copper matte, which is exported to the United States to be refined. Copper ores occur in great abundance, and constitute one of the most important mineral resources of the country. These are distributed over large tracts in Ontario, Quebec, Nova Scotia, and New Brunswick. The deposits consist of native copper and sulphides, the former confined principally to the Lake Superior region, the latter being more widely diffused, but notably in the Sudbury region, Ontario, where it occurs with nickel. The production of copper, other than the native copper near Lake Superior, is dependent for the most part on that of this latter metal. Some idea of the advances made in the production of copper matte may be had from the fact that in 1891 the production amounted to 9,000,000*l.*, while 1901 showed an output of 41,000,000*l.*[11]

Nickel.—The first discovery of nickeliferous deposits was made in 1883 near Sudbury, in the district of Algoma, Ontario. The ore, which contains on the average about 2·25 per cent. of nickel, is roasted in heaps, and smelted in a Herreshoff water-jacket furnace, near the mine, into a copper-nickel matte, the average composition of which is: copper, 26·91; nickel, 14·14; iron, 31·335; sulphur, 26·95; and cobalt, 0·935. It is also said to contain some ounces of platinum to the ton. Previous to the discovery of nickel in this country, the French colony at New Caledonia contributed the world's supply of the metal. Now the International Nickel Co. controls the deposits in Ontario and in New Caledonia, and has refining works at Hampden, N.J., in the United States.[12]

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[11] Statistical Year Book of Canada, 1901.

[12] The French Société le Nickel, with works in New Caledonia and refineries in France, is not included in this combination.

A partial list of firms engaged in nickel production is given in the Appendix. The Frasch and the Mond processes are the principal methods of treating the matte, that from the Victoria Mines of the Mond Co. being shipped to Swansea for treatment in England. The Frasch process for the separation of copper and nickel is an electrolytic one, and is being largely adopted here.[13]

Aluminium.—The extraction and refining of aluminium has in recent years, owing to the advent of electricity developed from cheap water power, become an important industry. At Shawinigan Falls, Quebec, are situated the Canadian works of the Northern Aluminium Co., a subcompany of the Pittsburg Reduction Co., which also has two large factories at Niagara Falls, on the American side. The raw material, bauxite, is obtained from Alabama and Georgia, in the United States. The process employed is the Hall[14] process, and is a combined electrolytic and electric furnace one. The native aluminium hydroxide is first purified by mixing with sufficient carbon to reduce all impurities in it to the metallic state, the resulting iron, mixed with titanium and silicon, forming a slag after melting the mass in an electric furnace. An alternating current of low voltage is used, and the purified alumina separates out above the slag in an almost chemically pure condition. The alumina thus purified is then electrolysed in a bath containing cryolite at a temperature of from 850° to 900° C. The action of the current sets free aluminium and oxygen, the latter uniting with the carbon anodes to form carbonic oxide. The metal is run into rough ingots weighing 20 lb. each, and is stated to contain, on an average, 99·5 per cent. of aluminium.[15]

The production at the Quebec works is probably 9,500 lb. per day, the value in 1902 being approximately 1,043,250 dols.[16] It may safely be said that the three works of this Company, between them, produce one-half of the world's supply.

Lead and Silver.—These metals are derived principally from the mines of British Columbia, but there are also deposits of galena along the shores of Lake Superior, the ore from which is sent to Niagara Falls, N.Y., for reduction.

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[13] U.S. Pat. 669,899.
[14] U.S. Pat. 677,207, 677,208, 677,209, of June 25, 1891.
[15] Dr. J. W. Richards in "Electro-Chemical Industry, Oct. 1902.
[16] *Ibid.* (average value of product is 31 cents per pound).

The British Columbia ore is a high grade one, carrying from 200 to 300 oz. of silver to the ton, and is mostly smelted at Butte and St. Helena, Montana. No refinery for lead (on a large scale) has yet been started in Canada, though at Trail, in British Columbia, the Canadian Smelting Works have recently begun to produce commercial lead, stated to be of 99·9 per cent. purity,[17] by means of the Betts process, which is an electrolytic one.

The Hall Mining and Smelting Works, whose Canadian headquarters are at Nelson, British Columbia, are smelting lead ores which are obtained in the Slocan and Kootenay Lakes. They employ blast furnaces, a considerable portion of the ore being first roasted in hand or mechanical furnaces and the product of the latter briquetted. The principal markets for the pig-lead are the Orient, England, and Canada, though the home market is somewhat handicapped by the present arrangement of duties, which allows the importation of foreign corroded lead at a lower rate than that imposed on pig-lead. With a revisal of the duties, a greatly increased development, and revival of the lead and smelting industries, is anticipated.[18]

In 1894 the amount of silver exported, in ores, concentrates, or otherwise, was 629,655 oz., while in 1901 the quantity had risen to over 4,000,000 oz.[19] Despite these figures, the "Monetary Times," Toronto, of date Jan. 16, 1903, says, "The silver-lead production of British Columbia is severely handicapped by the adverse competition of the United States, the European and Mexican products. The tariff is unfavourable—a higher one would be quite beneficial to the industry."

Arsenic.—A not unimportant metal found in considerable quantities in Ontario is arsenic; the chief form in which it occurs is arsenical pyrites (mispickel), which also contains gold. Its manufacture was begun by the Canadian Goldfields, Ltd., at their Deloro Mine, Hastings County, Ontario, in 1899. Attempts had been made, extending over the previous 20 years or so, to extract the gold from the ore found there, and, after the mine had experienced some vicissitudes, the present company acquired it and obtained the rights (1896) for Ontario to the Sulman-Tweed patents (bromo-cyanide process), working it with only a modified degree of success for a couple of years, when the installation

[17] Canadian Mining Rev., March, 1903.
[18] Letter from the Business Manager, Hall Mining and Smelting Co., Nelson, B.C.
[19] Statistical Year Book of Canada, 1901.

of improved machinery and the adoption of a combination of amalgamation and leaching with bromo-cyanide resulted in the recovery of arsenic from the mispickel concentrates. To accomplish this the concentrates are heated to a high temperature in specially constructed cylindrical revolving calciners, and the resulting impure arsenious oxide evolved is condensed in hermetically sealed brick chambers.[20] The crude arsenic is refined by sublimation, and contains from 99·6 to 100 per cent. arsenious oxide, the main impurity being silica in a finely divided condition.[21] It is exported chiefly to the United States, where it is used for making "Paris Green," &c. The output has increased from 113,477 lb. in 1899 to 1,347,000 lb. in 1901.[20] In time, and with proper development, Ontario should be able to supply the entire demand for arsenic on the continent of America.

Antimony.—This metal might almost be said to occupy the position of a by-product in the extraction of gold. At Rawdon, in Nova Scotia, the ore (stibnite) is auriferous, and from 1898 to 1901 no refined antimony was produced, the stibnite being mined for the sake of its more precious contents.[22] It is also found in Quebec, and recent reports indicate deposits of ore in several localities of Ontario and British Columbia. The output in 1891 had fallen to 60 dols. In 1902 the refining of the metal was renewed.

Gold.—Gold is mined to a small extent in Ontario, in in Nova Scotia, and Quebec. Gold deposits are also found in the Kootenay district, B.C., in Cariboo, B.C., and in the Yukon. In the Rossland district the ore is a cupriferous pyrrhotite under a diorite cap, and from Trail on the Columbia River, where the ore is smelted, the gold-copper matte produced is shipped to Montana for refining purposes. There is also a smelter at Nelson for the ore of the Hall mine. The Yukon territory covers in a general way

[20] C. Kirkegaard, in Eng. and Mining J., Jan. 31, 1903.
[21] Bureau of Mines Report, Ontario, 1901.
[22] Assays of two ores give, according to the Nova Scotia Mines Report, 1901 :—

	I.	II.
Antimony (per cent.)	45·75	18·21
Gold (oz. per ton)	2·48	0·23
Silver (oz. per ton)	0·10	0·13

the district north of Cariboo, south of the Arctic Ocean, and lying between the Mackenzie River and the Alaska-Canada boundary. Gold has been known to exist there since 1864, and has been worked intermittently since 1873. Forty Mile River, a tributary of the Yukon, was discovered to carry coarse gold in 1886, and, 10 years later, what is known as the Klondike was found to contain gold also. It was first discovered on Bonanza and Eldorado creeks[23]: the news of this discovery spread far and wide, and active prospecting was the result. There are about 1,400 miles of Canadian Yukon streams, on all of which gold can be found. Mr. Ogilvie, former Canadian commissioner in the Yukon, estimates that an area of 125,000 square miles is gold bearing.[24] The former difficulties of reaching the Yukon have now been overcome; a telegraph line has also been laid by the Canadian Government from Skagway, on the coast to Dawson. The gold is found and worked in the gravel deposits of the valleys and on their adjacent slopes, and it has been estimated that gold to the value of 95,000,000 dols. will be produced from these deposits in the next few years.[25]

The gold fields of Nova Scotia occupy the entire Atlantic coast line, and contain gold in combination with sulphides and arsenides of iron, but mostly in the free state. The table given in the next column will best convey the output of gold from Canada and its distribution.[26]

The gold production for the Yukon in 1902 was 12,018,561 dols.; according to the United States Mints it was 14,525,275.[27]

	1892.	1901.
	Dols.	Dols.
Ontario	7,118	243,022
Saskatchewan (N.W.T.)	98,006	15,000
Yukon	..	12,500,000[28]
Quebec	12,987	3,000
British Columbia	399,525	5,596,700
Nova Scotia	389,965	604,500
Total	907,601	24,463,222

[23] "Official Guide to the Klondike," by William Ogilvie.
[24] *Ibid.*
[25] Report of the Canadian Commission in the Yukon.
[26] Statistical Year Books, 1892—1902.
[27] Letter from Hon. Clifford Sifton, Minister of Interior Ottawa.
[28] Letter from Mr. B. E. Walker, General Manager, the Canadian Bank of Commerce.

III.—The Leather and Tanning Industries.

The manufacture of leather occupies quite a prominent position in Ontario and Quebec, the industry having greatly developed during the past few years. There are from 18 to 20 large establishments in operation, and fully 20 small ones. Bark, chrome, and combination tanning methods are employed, the spent bark being utilised as fuel in specially constructed furnaces. Though the United States may be said to lead the world in the extent of the leather produced, the quality of the Canadian product cannot be surpassed in heavy leathers for common goods. Light leathers, too, have made very creditable progress; also chrome kids and classes of bag, case, and trunk leathers. Much of the American patterned machinery employed, and formerly imported, is now being manufactured in the Dominion, such as bark mills, fleshing machines, glazing jacks, measuring machines, and leather presses. As compared with a decade ago, the value of the leather produced in the country may safely be said to have increased one half.

IV.— Sulphuric Acid, Acetic Acid, Wood Alcohol, Charcoal, and Ammonia.

The manufacture of commercial sulphuric acid has not yet been developed to the extent that the quantity of sulphur found throughout the Dominion would justify. There is enough sulphur in Canada to supply the entire home market with acid and even to develop a considerable export trade. Only a few firms, however, are engaged in the trade, and a large portion of their product is used in the refining of Canadian petroleum, some five million pounds being annually consumed for this purpose. Quebec, Ontario, and British Columbia are each represented in the acid industry. The Lake Superior Power Co. employs the sulphur obtained in the smelting of nickeliferous ores in the manufacture of sulphite pulp, but only utilises it as required for its own industrial operations. It is probable that the construction of electrolytic lead smelters will lead to the sulphur dioxide obtained from the galena being made into sulphuric acid, as is done at the Electric Lead Reduction Co.'s works at Niagara Falls, N.Y., where, it is stated, the sulphuric acid produced yields a financial return sufficient to cover the entire cost of the process.

By the destructive distillation of wood, acetic acid, wood-alcohol and charcoal are obtained; hence Canada, with its enormous supply of wood of all kinds, should be able to

take a prominent place in the production of acetic acid and wood spirit. At the present time the residual charcoal from the retorts does not find a ready market, owing to the comparatively high rates for transport as compared with other fuels, weight for weight. The outlook in this direction is, however, brightening. Among the firms engaged in this manufacture might be mentioned the Standard Chemical Co.—with plants at Fenelon Falls, Deseronto and Longford, Ontario, and Cookshire, Quebec—and the Canada Paint Co., Montreal and Toronto. Very keen competition has to be faced in this connection with the United States, as a combination of some 175 manufacturers practically controls the market. The crude acetate of lime produced in the distillation process is converted into acetic acid, some of which is sold for dye and colour making purposes, while a considerable portion is exported to Europe and Australia.

The wood alcohol, obtained at the same time as the acetic acid, supplies the home market and is also exported largely to great Britain, France, Germany, Holland, Japan, and Australia. It may be of interest to know that timber is imported from Canada by makers of wood-alcohol in the United States.[29]

V.—Soap and Glycerin.

Soap.—The soap industry in Canada is growing rapidly ; at the present time some 15 large concerns are in operation, employing in all about 2,000 hands. A branch of the well-known firm whose headquarters are at Port Sunlight, near Liverpool, was recently started in Toronto, with an annual capacity of 10,000 tons. Their products are similar to those made at their other works, and their raw materials are procured from Africa, the United States, and locally (tallow). They own islands in the Pacific from which they import cocoanut oil.

Most of the other firms mentioned in the Appendix are also manufacturers on a large scale and produce all grades, from the cheapest textile and laundry soaps to the finer qualities of toilet soaps. Great advances have taken place in the industry during the past 10 years, particularly in the making of the latter. The same system of manufacture obtains as in England. The raw materials are mainly cocoanut oil, palm oil, and tallow, the first two in a large

[29] Mr. Webster, of the Standard Chemical Co.

measure superseding the last mentioned. The market for Canadian made soap is limited, the home market is supplied and a large export trade is done with the West Indies and Australia. The competition of the United States is felt more than that of England or France. In 1902 the value of the soap produced was approximately 3,000,000 dols.[30]

Glycerin.—This necessary by-product in the manufacture of soap is refined in some cases by the producers themselves; others sell it to firms engaged more particularly in the refining trade. Among these might be mentioned the St. Henri Chemical Co., of Montreal, who buy waste lyes from the soap manufacturers, recover the salt from the lye, refine the glycerin and sell to the makers of nitroglycerin. The capacity of these works is 10,000,000 lb. of waste lye yearly.[31]

VI.—Refined Chemicals and Drugs.

One is reminded forcibly, after writing the heading to this section, of the "Snakes in Ireland" story, and, indeed, the classical remark recorded on that occasion might almost be said to apply with equal force to the refined chemicals produced in the Dominion. Messrs. Lyman Bros. and Co., of Toronto, however, are conspicuous in having their own laboratories, in which are made some 150 salts, acids of phosphorus, syrups, tinctures, and flavouring extracts. Most of the raw materials are imported. The scope of the business is increasing yearly. The production of chemicals in 1892 amounted to 37,000 dols., and last year had increased to 50,000 dols. The small demand for pure chemicals is mainly accountable for the lack of local manufacturers, the market being necessarily a small one, and most buyers of pure chemicals for laboratory uses are apt to demand articles of the make of one or other of the large and old-established German or English houses. One can hardly doubt but that the Canadian maker must desire a higher tariff on imported material. Within the last year the Liquid Carbonate Co. — and liquid carbon dioxide *is* made in Canada, and used largely in the manufacture of aërated waters—have been making Epsom salts and Glauber's salt as a by-product, while pepsins and phosphates, mainly for medicinal purposes, are now produced by the William Davies Co.

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[30] Mr. Knight, of the Sunlight Soap Co.
[31] Letter from the President of the Company.

VII.—Fertilisers.

Mineral phosphates, in the form of apatite, are found in the Ottawa Valley, Ontario, but the deposits have not been worked for several years. About 1891, in which year the phosphates mined were valued at 50,000 dols., a falling off began in the output of this mineral, which has continued up to the present time, the amount now mined being hardly worth recording. This state of affairs has been brought about mainly by the large supply of easily-worked phosphates found in Florida and Carolina, U.S.A., much of which is obtained by dredging. It may be mentioned, however, that a certain amount of apatite is made use of in the Province of Quebec by the Buckingham Electric Reduction Co., who manufacture phosphorus therefrom.[32]

Sulphate of ammonia is manufactured at the works of the Dominion Iron and Steel Co., Sydney, N.S., whose products are supplied to dealers and others engaged in the fertiliser business. The ammoniacal liquors of the Quebec, Ottawa, and Toronto Gasworks are worked up at the latter city by the Michigan Ammonia Co.[33] In Montreal, one firm, at least, makes sulphate of ammonia, and at one time the gasworks there utilised their own liquors for its production. Latterly, however, the gas liquor was exported, to be dealt with by a firm in the United States.

Quite a number of other fertilisers are produced in the Dominion from refuse matter, such as blood, tankage, bones, and offal, besides natural phosphates. Ontario, New Brunswick, Quebec, Nova Scotia, Prince Edward Island, and British Columbia, all produce fertilisers, more or less.[34]

VIII.—Coal-Tar and Asphalt.

Very little tar distillation is carried on in the Dominion, owing to the tar produced in the gasworks being too thick for treatment with any degree of success. It is mainly used for saturaturing paper, which is employed largely as a waterproofing material by builders. Some is boiled down into pitch, but fully one half of the tar produced is exported to the United States. There is a small distilling plant at Hamilton, Ontario, which, the writer understands, is at

[32] Minerals of Quebec; published by the Prov. Government.
[33] Letter from Mr. Macfarlane, Chief Analyst to the Inland Revenue Department.
[34] Inland Revenue Bulletin, No. 81, 1902.

present the only one of its kind from which coal-tar oils are produced in Canada.[35]

Asphalt.—Asphalt occurs naturally in several varieties as albertite, found in King's and Albert Counties, N.B., and as maltha, one of the stiffer petroleum compounds, which is not of much importance, however, being almost too hard for use in street paving. Up to 1898, albertite was employed in gas-making, and much of it was shipped to the United States, but the original supply is now exhausted.

IX.—Calcium Carbide, Carborundum, and Graphite.

Calcium Carbide.—The production of this substance on a manufacturing scale dates back only to the year 1891, when Mr. T. L. Willson, of the Willson Aluminium Works at Spray, N.C., accidentally obtained carbide whilst trying to reduce lime by carbon in the electric furnace. Instead of metallic calcium resulting—which was to be employed in preparing aluminium—a hard, almost black, substance was obtained which reacted violently with water, giving lime and an inflammable gas clearly recognisable as acetylene. The author was privileged, through the courtesy of Lord Kelvin, to have at one time in his possession some pieces of the first carbide made by Mr. Willson at Spray. Acetylene being a powerful illuminating agent and readily obtained from carbide, the development of the carbide industry on a commercial scale followed this discovery as a natural consequence. The industry has progressed by leaps and bounds during the past decade, in Europe even to the extent of over-production.[36] Two carbide works are in operation in Canada, using water as their source of power, namely, the Willson Carbide Co., at St. Catharine's, Ontario, and the Ottawa Carbide Co. The Union Carbide Co.[37] of Chicago, which utilises 13,000 horse-power in all and has an immense establishment at Niagara Falls, N.Y., has contracted for a large amount of power for a new plant at Sault Ste. Marie, Ontario, for the manufacture of carbide.[38] Another important prospective company is the Shawinigan Carbide Co. of Shawinigan Falls,

[35] See Section II., Iron and Steel.

[36] Italy alone possesses enough carbide plants to supply the whole of Europe. Dr. J. W. Richards, in "Electrochemical Industry," Sept. 1902.

[37] Capitalised at 6,000,000 dols. On the American side of the river.

[38] "Electrochemical Industry," Dec. 1902.

Quebec,[39] the works being now in the course of construction. The process of manufacturing consists in fusing together burned lime and ground coke in the electric furnace; the temperature required is not so high as that needed in other operations for which the electric furnace is employed, notably the making of carborundum and graphite. The reaction taking place in the furnace results in a transference of the oxygen of the lime to a portion of the carbon with the formation of carbon monoxide and carbide of calcium.

The present market value of carbide (61 dols. per ton)[40] affords considerable profit to its manufacturers, and the increasing popularity of acetylene as an illuminant ensures a brighter future for the industry. In Ontario several towns have already had acetylene installed for house and street lighting, the gas being generated at a central station and distributed in pipes to the consumers.[41] At the generating station the gas is purified by a special process before use, which obviates all the disadvantages inseparable from the employment of small generators—automatic or otherwise—by individuals, who in most cases have neither the time nor the scientific skill necessary for the proper production of the gas, simple as it may appear at first sight.

Carborundum.—Ten years ago the very name "carborundum" was unknown; it is due entirely to the advance made in the development of electrical power, obtained from the immense waterfalls of the American Continent, that this as well as other materials are now in daily use throughout the world. Although deposits of corundum itself are found in Eastern Ontario, the artificial carbon silicide has practically supplanted the natural product as an abrasive agent. The history of carborundum may well be likened to that of carbide, its discovery being accidental. A full account of this interesting substance will be found in a paper by the Chairman of the Liverpool Section (Dr. Kohn) in 1897 (see this Journal, 1897, 863).

The Canadian works of the Carborundum Co. are comparatively small, only operating 200 horse-power. The factory, however, supplies the Canadian market, thus avoiding the payment of duty. The writer is informed by

[39] Capitalised at 1,000,000 dols.

[40] Ontario Mines Report, 1901.

[41] Worked under patents held by the Burgess Gas Process Co., Canadian Pat. 73,040, Sept. 10, 1901; Eng. Pat. 241, Jan. 3, 1901; Amer. Pat. 701,995, June 10, 1902.

Mr. Acheson that most of the Canadian product is exported to Scotland, to be used there in finishing granite. The estimated cost of the crude crystals is 2·5 cents per pound, that of the treated powder, 4·5 cents per pound, while the selling price averages 9 cents per pound.[42]

Graphite.—Though no company for the manufacture of graphite has yet been capitalised in Canada,[43] the production of it by the Acheson process is carried on to a small extent in the Canadian branch of the Carborundum Co. at Niagara Falls. The formation of the "skeleton" crystals suggested making use of the decomposition of carborundum for making graphite itself. The inventor's patents include the production of graphite in the form of pure electric-light carbon, by subjecting impure carbon to a high temperature for a sufficient length of time to volatilise the impurities;[44] the conversion of carbon into graphite by mixing with it such metallic oxides as would be capable of forming metallic carbides, to be subsequently decomposed;[45] the conversion into graphite of such natural carbonaceous material as contains, uniformly intermixed through it, metallic oxides sufficient to produce carbide, and thence graphite.[46] These processes throw considerable light on the scientific principles underlying the formation of this substance.[47]

X.—*The Cement and Plaster Industry.*

The manufacture of Portland cement is mainly confined to Ontario, though one establishment—the Crescent Cement Works—is situated at Longue Pointe, in the province of Quebec. In Ontario there are some 14 companies, and eight factories in operation, and throughout this Province are found the necessary raw materials (clay and marl) of an excellent quality. The development of the industry has been rapid, and has all taken place within the past few years. The most improved method of procedure is as follows: the marl is thoroughly mixed, mechanically, with water into a thin paste, and the same operation is performed with the clay. The two fluids are mixed thoroughly in the

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[42] U.S. Pat. 542,982 of July 23, 1895.
[43] Letter from Mr. Acheson.
[44] U.S. Pat. 542,982 of July 23, 1895.
[45] U.S. Pat. 568,323 of Sept. 29, 1896, and No. 617,979 of Jan. 17, 1899.
[46] U.S. Pat. 645,285 of March 13, 1900.
[47] Electrochemical Industry, Vol. I., No. 2.

required proportions, and in a pasty condition are pumped into rotary steel calciners, about 70 ft. in length and 6 ft. in diameter, set at a slight angle to the horizontal. These rotary calciners are the great feature of the Canadian cement plants. This form of kiln is originally of English origin, but has only been brought to its present effective condition since its introduction to this country. In the interior of the kiln are "channel-irons" running from end to end. At the lower end fuel is introduced in a particular manner, and the burning gases pass through the entire length of the kiln, and are allowed to escape at the upper extremity. At this latter end is introduced the "slurry" of the mixed ingredients, which becomes dried and finally calcined in the slow passage from one end to the other. The revolving irons carry the "slurry" up with them as they rise, and on reaching the top it falls, under the action of gravity, through the burning gases, being subjected at the hottest part to a temperature of 3,000° F., when combination takes place between the constituents of the fused mass, and the resulting "clinker" emerges into the vessel destined for its reception. The drying and calcining is thus performed in one operation, and no preliminary pressing of the material into bricks is required.[48] At the works of the National Portland Cement Co., recently erected at Durham, Ont., a great saving of time is effected by cooling the clinker in vessels drawn by an endless chain through a stream of water below the ground level. After cooling in this manner it is ground to a fine powder, and packed in bags or barrels ready for use. The whole operation by this process occupies only eight hours, a period of time which will be appreciated by all aquainted with the older methods. At Durham the raw materials are brought from the natural deposits, which are close at hand, calcined, cooled, ground, and packed by means of a continuous series of mechanical conveyers, from one part of the establishment to the other. This company has another plant in course of erection at Hull, P.Q., on the Ottawa River, which is intended to supply the Eastern Canadian market.

Several articles have appeared lately in the public press,[49] pointing out that a possible over-production of cement may be the result of the numerous large concerns which are

[48] The Portland Cement Industry: "Queen's Quarterly," Jan. 1903.

[49] "The Globe," Toronto, March, 1903, and other papers.

already in operation, or are about to be started. Whether or not this will take place in the immediate future depends, naturally, on the general prosperity of the country and the consequent demand for building materials. Certainly cement has gained considerable reputation as a substitute for stone, as can be seen by the extent to which it is made use of by architects. It can be readily moulded into any form and may then be dressed to represent the natural article. Whether it can ever oust stone or brick from their present position depends, not only on its comparative cost, but on the quality of cement put out by manufacturers. One case of a collapse due to an admixture of a single bag of inferior material and the whole fabric of the cement industry, as supplying a substitute for the older building materials, will be in danger of a similar fate. The total output of Portland cement in 1902 was valued at 1,028,618 dols.[50]

Gypsum is found in considerable quantities in Nova Scotia and New Brunswick. At Windsor, N.S., there are immense deposits; the beds found in the vicinity of Hillsborough, N.B., are, however, very large and of great purity, and form the basis of the most extensive operations.[51] It is also found in Ontario, and plaster works are located at Paris in that province. In 1901, active operations were begun at Gypsumville, Manitoba. The industry, however, is principally located in New Brunswick. Drawbacks in the way of freight charges, inadequate shipping facilities, and the competition offered by manufacturers of plaster of Paris in the United States, kept the industry from developing until the Intercolonial Railway was opened and the increased duty on American plaster imposed, when the New Brunswick plaster, quarried and prepared at Hillsborough, came to be firmly established on the Canadian market. In manufacturing plaster of Paris, the stone is first dried in the air and ground—not burned in lumps, as is still done to a considerable extent in England and on the Continent of Europe—and the pulverised material subjected to a process of calcination in kettles, of a capacity of 60 barrels of 300 lb. of the calcined plaster, furnished with lids and stirring arms which keep the material in constant motion. When the required temperature has been reached (285° F.), the

[50] Geological Survey of Canada: Mineral Products, 1902.
[51] Geological Survey of Canada: The Mineral Resources of New Brunswick, 1899.

plaster is removed and packed in paper-lined barrels for market. Analysis of the Hillsborough gypsum shows it to contain 99·88 per cent. $CaSO_4$.[52] The principal markets for plaster of Paris are Canada, the United States, and South Africa, while the crude gypsum is exported largely to New York and other portions of the States, being used for making plaster for walls and ceilings.[53] According to the Geological Survey Reports for 1902, the gypsum produced in Canada during that year amounted to over 332,000 tons, valued at 356,317 dols.

XI.—Carbohydrates: (a) The Refining of Sugar; (b) The Beet-Sugar Industry.

Refining of Raw Sugar. — The recent remarkable developments in the production of sugar from beets in Ontario and Southern Alberta have rather minimised the importance of the refining of imported sugars in the Dominion, and there seems little reason to doubt that the beet-sugar industry will continue to progress, as will be seen from the sequel. Statistics show that, during the last decade, cane sugar has increased in production about 200 per cent. Judging from present appearances, and allowing for some slight tariff alterations, the increase in Canada should soon be in proportion to that of other countries.[54]

Raw sugar is imported from Cuba, the West Indies, Java, Manila, the Brazils, Mauritius, and the Continent of Europe. The most improved machinery and processes are employed, refined sugars and syrups being the staple products.

Belgium supplies to Canada the largest proportion of sugar, the imports from that country amounting in 1901 to 127,931,553 lb.; from Germany in the same year 83,941,290 lb. entered the country, the total imports being 336,694,833 lb., valued at close on 8,000.000 dols.[55]

Beet Sugar.—The most interesting point connected with the sugar industry is the remarkable way in which the production of sugar from beets cultivated on Canadian soil has become, in the past few years, an important factor in

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[52] Analysis by A. A. Breneman, of New York, in Mineral Resources of New Brunswick, Geological Survey of Canada, 1899.

[53] Letter from the Manager, Albert Manufacturing Co.

[54] Letter from Mr. D. A. Gordon, President of the Wallaceburg Sugar Co.

[55] Essay, Mr. Read, University of Toronto.

the country's progress. As far back as 1872 the Dominion Government sent a special agent to Europe to make a study of the industry. A bounty of 25,000 dols., afterwards increased to 70,000 dols., was offered by the Quebec Government in 1875 to the first successful factory to be established in a situation approved by the Government. This led to the establishment of a company, known as the Union Sucrière du Canada, which, in 1881, erected the first of four proposed factories at Berthierville, Que.[56] This establishment was unsuccessful and only operated for a few days, mainly owing to the failure of the beet crop. After passing into other hands the plant was bought by an American company and removed to Eddy, New Mexico.[57] Another company was, in the same year, organised at Farnham, P.Q., not far from Montreal, which, after some vicissitudes, did not deem its success sufficient to warrant a continuation of its operations, so sold its plant to a company at Rome, N.Y., in 1897. A third company, known as the Pioneer Beet Co., started operations in 1881, at Coaticook, P.Q.,[57] and was successful in part, receiving a subsidy of 35,000 dols. from the Government, but it, too, closed its doors in 1883. The causes to which these failures may be attributed were lack of capital and enterprise, and the indisposition of the farmers to cultivate beets. The Agricultural Departments of the Provincial Governments, however, continued experimenting with various kinds of beets and studied the conditions most favourable to their successful growth. For some years past the Ontario Agricultural College at Guelph has, as a consequence of the excellent results obtained at their experimental stations, been carrying on an educational campaign among the farmers of the province. As a result of this the quality and tonnage of beets now grown in different parts of Ontario surpass those of many American States. The climate of this province, with its sunshine and long autumns, is peculiarly favourable to the cultivation of the beet, which takes about four months and a half to reach maturity. It requires, however, to be demonstrated to the farmers that the cultivation of beets will pay them better than other land produce before the requisite supply of suitable material will be obtained. That profits are large can be gathered

[56] Report of Dominion Government on beet sugar manufacture in Canada.

[57] Letter from the manager of the Dresden Sugar Co., Ontario.

from the fact that wheat yields in Ontario 15 dols. an acre per annum, oats, 9·74 dols., and beets for sugar, 60 dols. In the last case the cost of production is necessarily large, owing to a greater amount of labour being required, but, all the same, the profits to the farmer should, with skilful treatment, be at least 30 dols. per acre per annum. The beet tops are of value as a fertilising agent owing to the salts they contain, and find a use also as a food for cattle. In 1901 beets were grown—under instructions from the Agricultural Department—in 15 districts of Ontario, and the average yield per acre was over 17 tons of a high quality of beets which gave an average of 15·6 per cent. of sugar of an average purity of 87·7 per cent. All this points to a great future for Ontario as a sugar-producing country; this important fact has been fully realised by the Provincial Government, which has offered a bounty of 275,000 dols. for three years,[58] to be distributed among factories according to the amount produced. Four companies have been organised lately, namely, the Wiarton Beet Sugar Co. (capital 445,000 dols.), whose works are situated on Lake Huron, with a capacity for treating 350 tons of beets per day; the Dresden Sugar Co., capacity 600 tons; and the Ontario Sugar Co., at Berlin, the last with a capital of 1,000,000 dols.; each of these companies has received a bonus from the town where it is situated, averaging 28,000 dols. The capitalisation of a company engaged in this industry depends entirely on the size of the plant, a general estimate of 1,000 dols. per ton of beets per day may be considered a fair calculation of what would be required.

Beet sugar factories have also been established in Alberta, in the North-West Territories of Canada. Since 1898, an area of about 300,000 acres has been made productive by means of the irrigation system of the Canadian North-West Irrigation Co., and a portion of this area has been utilised for beet cultivation, principally by the Mormon settlers. The most important factor is now in course of construction at Raymond, south of Lethbridge, on the Canadian Pacific Railway. The capital of this Company is 1,000,000 dols. The area intended to be planted with beets is 3,000 acres, and the daily capacity of the factory will be 400 tons of beets per day. The only difficulty which the industry is encountering in the north-west is the scarcity of labour.[59]

[58] 1 Edw. VII, cap. 11, 1901.
[59] Letter from Manager of works at Raymond.

This is due partly to the scanty settlement of the country, and partly to the superior attractions of the mining regions, which are situated at no great distance.

A plentiful water supply, lime, and a source of power, are necessary for the profitable prosecution of the industry; all this has been carefully considered in locating the factories enumerated above, steam power being employed for pumping and the working of all machinery: There is room for many more factories in the Dominion; according to Dr. A. B. Shuttleworth, Chief Agriculturist to the Ontario Sugar Co., whose name is indissolubly connected with the development of beet cultivation, it would require over 30 refineries of 600-ton capacity to supply the home market alone.[60]

The working season of a factory runs for about 100 days, operating continuously. The cost of the sugar is from 3 to 3½ cents per lb. and the profits to the makers are estimated at 50 cents per ton of beets used. This would mean that in a factory of 500 tons capacity, working for 100 days, the profits would amount to 25,000 dols.

The scope of this article does not allow of any detailed consideration of the working process by which the sugar is extracted from the sliced beets and crystallised. New processes are being employed for utilising the residual molasses. This is treated for the recovery of the sugar in some part, and also for the production of alcohol by fermentation. An American company in 1901 produced 915,000 galls. of alcohol in this way, of a quality considered to be quite equal to the grain product. Another new process is that of the manufacture of syrup from the beet instead of sugar: 40 galls. of this can be obtained from a ton of beet, which, at 30 cents a gallon, means a return of 12 dols. per ton of material used, while the product in sugar yields only from 7 to 8 dols. per ton of beets. The beet pulp refuse is also being largely used as a food for live stock, for which purpose it is extremely suitable owing to its nitrogen contents. In this connection a new process has been introduced for drying the pulp, which entails an expenditure of 5 dols. per ton, but, as the dried pulp is sold at 6·25 dols. per ton, a clear profit of 1¼ dols. is thus secured to the manufacturer.[61]

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[60] Berlin News Record, Nov. 8, 1902.

[61] In the above I have drawn largely from an essay on the beet-sugar industry by Mr. E. R. Read, a fourth year student in the Department of Political Science, University of Toronto, who kindly placed his papers at my disposal. Also from Dr. Shuttleworth's article in the "Berlin News Record."

The production of sugar from Canadian grown beets is a new and rising industry which offers great scope for some co-operative arrangements between the companies and the farmers. It should give an impetus to agriculture, afford employment to thousands of unskilled workpeople, and, as an important industry, be a lasting benefit to the country. The following communication, dated March 6, 1903, from Mr. George Elsey, manager of the Dresden Sugar Co., conveys some idea of the position of the industry at the present moment and its possible future :—

"At the present time there are four factories which operated this last season, and, from what we are able to learn, the results were as satisfactory as could be expected under the existing conditions, that is, the rainfall last summer damaged the beet crop from 50 to 60 per cent., both in the United States and in Canada. The balance of the crop, on account of wet weather, cost considerably more to raise than what was necessary. It was unfortunate that this should occur in the first season that the factories were started in Canada as it was very disappointing, but most of the farmers have told us that they were surprised at the amount of rain the beet would stand, and in several instances where they could harvest the beet crop, the corn and other crops were ruined. After we have had a seasonable year, and it will be demonstrated to the farmers that there is more money in raising sugar beets than any other crop that grows, the four factories now in existence will get their supply of beets within hauling distance of the factories. . . . Our farmers know well that the Michigan farmers obtain about a dollar a ton more for their beets than they do, and they also understand that it has cost as much in money and labour to raise a ton of beets in Canada as it does in Michigan or any part of the United States. They therefore feel dissatisfied, and are clamouring for more money, which the companies would be glad to pay if they could sell their sugar for the same price as the American Beet Sugar refineries. The difference between the two markets to-day is 1·10 a 100. The present Canadian sugar tariff is such that it would not allow any more sugar refineries to be built in Canada. The companies that are already here have the experience of what this tariff can do. It allows sugar that has been refined in the United States to be shipped in here and undersell Canadian refined sugar, which means a loss to the refineries and to the Canadian people. It allows raw beet sugar to be im-

ported at a price that will prevent the farmers from taking hold of the beet industry as they should. Canada is sending to Germany and other foreign countries about 1,000,000 dols. per month for raw beet sugar, and the naturally yearly increase of consumption is about eight per cent., so that the future of the sugar beet industry, under a proper tariff, would be a lasting one and a great benefit to the farming community."

XII.—Natural Gas and Petroleum.

Natural Gas.—The existence of natural gas in Ontario was first discovered in 1889, being found in two well-defined areas, as the Essex county field and the Welland county field. It is chiefly near Buffalo, on lake Erie, and near Windsor, Ontario, that the largest supplies are met with, though practically it may be got in nearly any part of the Niagara peninsula in small quantities. In 1901 there were 158 wells in operation, and 368 miles of piping were needed to distribute the gas. Much of the gas produced in Essex county was formerly led across the river to Detroit by pipe lines, but on representations made by the people of the Essex district, to the effect that the supply of gas was not sufficient for home consumption, the Ontario Government passed an Order in Council, in October 1901, prohibiting the gas from the Essex field being exported to the States. None of the product of this natural gas field is therefore now being sent across the Detroit river; it is, however, still exported from the Welland field to the American side of the Niagara river, chiefly to Buffalo, N.Y. It may be mentioned that the landowners on whose farms the wells are located get their gas free in addition to being paid for the use of their land.[62] The value of the gas produced in Ontario during the last ten years shows considerable fluctuations, being somewhat less in 1901 than in the previous year, due, no doubt, to the Government prohibiting its export.[63]

Petroleum.—This is one of the chief mineral products of the Dominion, though as yet the output is not sufficient to meet Canada's needs. The principal seat of the industry is at present in Ontario, where commercial quantities are found in the counties of Kent and Lambton. In the former there are two oil fields, one at Oil Springs, extending over 1,200

[62] Report of the Bureau of Mines, Ontario, 1902.
[63] Statistical Year Book of Canada, 1901.

acres, and the other in the Petrolea district, 20 miles long by 2 wide.[64] In Lambton county the industry dates back to the year 1862. Petroleum is also found in Quebec, Nova Scotia, and New Brunswick, and boring operations that have in recent years been carried on at Athabasca, near Edmonton, in the North-West Territory, point to a likelihood of that part of the country contributing largely to the future supply of mineral oil.

The industry is now one of the most highly organised in the Dominion; the system of drilling and pumping now used—the "jerker-line" system—enables a well yielding from eight to ten gallons a day to be profitably worked. This system has gained for itself a world-wide reputation; it is used in Galicia, Russia, Afghanistan, Burmah, India, Italy, France, California, and Australia. Its advantages are numerous: a central engine can operate a large number of wells; on one property near Petrolea, 233 wells, scattered over an area of 400 acres, are worked by a single engine. It is estimated that to sink a well of about 500 feet in depth costs only 125 dols.[65] In 1900, there were approximately 10,000 wells in operation, yielding on an average 71 barrels of oil each.

The refining side of the petroleum industry is largely in the hands of the Imperial Oil Co.,[66] which some years ago absorbed several other concerns, and of the Canadian Oil Refining Co. The plant of the former at Sarnia has a capacity of 60,000 barrels of crude oil per month, and the market for their products reaches from Halifax to Vancouver. Many of the bye-products of the refining process find a market in England and in Spain. The latter company have erected an up-to-date plant at Petrolea, on the site of one which was in operation some years ago, where all the products will be manufactured that modern science shows can be obtained from petroleum.[67] Improvements in methods of retorting have recently led to a considerable quantity of the crude oil being used for gas making, $3\frac{1}{2}$ million gallons being an estimate of the amount so employed.[67]

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[64] The oil is found at depths varying from 370 to 400 feet.

[65] This, and much of what is given here on natural gas and petroleum, is from a paper by Mr. J. W. J. K. Vanston, read before the Canadian Section of the Society of Chemical Industry in Jan. 1903.

[66] Capital stock, 1,000,000 dols.

[67] Bureau of Mines Report, Ontario, 1902.

There has been a slight falling off in the production of oil during the past years: calculated as "crude" oil, the output in 1891 was 27 million imperial gallons, and in 1901 a little over 26½ million.[68] A slow process of diminution seems to be going on in the area at present productive, and a falling off must be looked for from year to year unless this is counteracted by an extension of the oil-bearing territories.[67] Probably, the field about to be exploited in the North-west will alter the position somewhat, and an increase in the output may be confidently looked for.[69]

XIII.—Pulp and Paper.

Pulp.—As timber is one of the chief natural products of the Dominion, it is only to be expected that Canada should figure largely in the wood-pulp industry; the figures that might be given to indicate the number of cords of pulp-wood available throughout the country are so large that one could hardly grasp their real significance. The industry is not so young as many others that have been considered: in the census of 1871, no pulp-making plants are mentioned; in 1881, there appear five mills, employing 68 men, and having an output valued at 63,000 dols.; in 1891 there were 24, with a yield valued at more than a million dollars; while 1901 shows some 35 factories from which the exported pulp alone amounted to nearly 2 million dollars.[70] The area of pulp-making operations is not confined to any one province, New Brunswick, Nova Scotia, Quebec, Ontario, and British Columbia all being represented in the industry.

The principal woods employed for pulp-making are white and black spruce, balsam, poplar, and pine; spruce[71] and balsam are those most generally used, on account of the special quality of their fibre and their colour, pine being utilised mostly for chemical pulp. The two main varieties of the pulp are *mechanical* and *chemical*. The

[68] Statistical Year Book, 1901.

[69] Total value of products of petroleum in Ontario in 1901, 1,467,940 dols. Bureau of Mines Report, 1902.

[70] Statistical Year Book, 1901.

[71] In 1894 it was estimated that Canada contained between 38 and 40 per cent. of woodlands and forests, or about 1,400,000 sq. miles, one-half of this being spruce. The spruce area is thus 450 million acres. In all there are 4,500 million tons of pulpwood in sight. ["Pulpwood of Canada." Pan-American Exhibition pamphlet, published by the Geological Survey, 1901.]

former is obtained by grinding spruce logs to powder, the logs being pressed against a rapidly revolving grindstone, with water constantly supplied to prevent the friction causing a rise of temperature. A liquid pulp is thus obtained from which the water is squeezed by hydraulic machinery, a pressure of many tons to the square inch being employed. The resulting pulp still contains water, however, to the extent of from 50 to 60 per cent., though some works—notably those at Sault Ste. Marie—have introduced a machine specially constructed for the purpose of removing this large excess of moisture. Where the pulp is to be made at once into paper, this drying process is unnecessary. The specially dried pulp resembles paper very closely in outward appearance.[72] Chemical pulp is prepared by disintegrating and extracting the resinous matter from the wood—in the form of chips—by digestion with sulphur compounds, usually a weak solution of sulphurous acid, about a quarter of which is in the form of bisulphite of lime.[73] A soda chemical process is also employed by some makers. The sulphurous acid is either made from sulphur imported from Sicily, or obtained by burning pyrites. Chemical pulp possesses many advantages over mechanical pulp, though its manufacture is necessarily more expensive, and the yield per cord of wood, as compared with the latter, is much less.[74] It has a longer and tougher fibre, and, the resinous matter being no longer contained in it, finds uses for qualities of paper for which the mechanical pulp would be unsuitable. The principal markets for pulp are Great Britain, the United States, France, Australia, and Japan. Much of it is used, however, locally for the manufacture of paper.

Paper.—In many cases the producers of pulp also manufacture it into paper. The principal requisites for the paper industry are a plentiful supply of pulp-wood, good water and an abundance of it, and cheap power; all these can be found in many parts of Canada. The growth in the demand for paper of all kinds, news, wrapping, wall, and the finer grades, was one of the features of last century—especially news paper. The introduction of wood fibre into

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[72] The Saulte Ste. Marie Works use some 200 tons of spruce logs, yielding 150 tons of pulp per day.

[73] Letter from Mr. Carl Riordan, Merriton, Ont.

[74] One ton of mechanical pulp requires a little over a cord of wood; 1 ton of chemical pulp requires a little over two cords of wood.

its manufacture has consequently enabled the supply to keep pace with the demand. The process of manufacture requires no description here; the secretary to a prominent Canadian firm states that originally they used rope as a raw material, then straw, which was abandoned for rags, and finally these gave place to chemical and ground wood-pulp. Previous to 1870 no wood whatever was used in the manufacture of paper in this country. Ground wood-pulp was introduced at that time, and has become the filling material of the cheaper grades of paper, being partly pasty and partly fibrous. Up to 1885 the real fibre—the framework of the paper—was supplied by rags. In 1885 sulphite pulp was introduced and has largely replaced rags, except in the higher grades of paper, in which linen is used, and in the very low grades, where straw is employed.[75]

The "Toronto Globe" of March 4th, 1903, in an article on the wood-pulp industry, gives the following statistics, which are of interest:—

	Tons.
Production of mechanical pulp in 1902	155,210
„ sulphite „ „	76,735
„ soda „ „	9,044

XIV.—Asbestos.

This mineral occurs in large deposits in the "Eastern Townships" of Quebec, where it was first worked in 1878; from 1880 up to the present date the production of asbestos has increased steadily; the output that year is given as 380 tons, while in 1901 over 38,000 tons are recorded in the return furnished by the producers. The world's supply of asbestos is, for the most part, obtained from Canada, and the Quebec deposits have in the past proved to be the most profitable mineral mined in the province. Thirteen mining companies are at work in this industry, which is principally carried on at Thetford, Lac Noir, and Danville,[76] giving employment to approximately 1,000 men. Asbestos is shipped largely to Great Britain, the United States, Belgium, Germany, and France.

Another silicate found in Canada is mica, which, though occurring in small quantities, is a not unimportant industry;

[75] Mines Report, P.Q., 1901.
[76] See note 73.

in Ontario there are several mines and a number of works where splitting, trimming, and sorting the mineral into saleable sizes is carried on. Most of these, however, are on a small scale.

Conclusion.

The subjects that have been considered in this paper do not by any means exhaust the catalogue of chemical industries in Canada. Many important manufactures have, for the reasons mentioned in the opening paragraph, been omitted. A short summary of these will suffice. Matches, for example, constitute an important and necessary article of daily use, and are made in enormous quantities, practically all that are used in Canada being manufactured in the country. Brewing and distilling are also carried on extensively, ale, lager beer, and stout being made, while Canadian rye whiskey is known throughout the whole English-speaking world; even a "Canadian Scotch" is produced at Perth, Ont.; brandy and champagne and other wines are made at Hamilton, Brantford, and Pelee Island, on Lake Erie. Fruit canning is one of the great industries of Wentworth and Essex counties, Ont.; bacon packing and salmon canning may also be classed among those manufactures requiring the careful supervision of the skilled chemist. To the list may be added explosives of all kinds; blackings, varnishes, japans, lacquers, paints and shellac, foodstuffs and sauces; antitoxins for use in the practice of medicine are made by the Parke Davis Co. at Walkerville. Natural mineral waters are abundant at St. Catharines in British Columbia, and in Quebec, while manufactured aerated waters are made in nearly all the important towns. The almost universal wearing of india-rubber foot coverings during the winter season necessitates the production of large quantities of goods of this sort. Many large factories for this purpose are in existence, from which rubber goods of a superior quality emanate; dyeing and calico-printing might also be mentioned as being in a flourishing condition. The attitude of manufacturers towards chemists has of late years been extremely favourable and many have seen it to be to their advantage to employ men trained in our universities to investigate the processes and materials employed in their particular industries. So far their employment has been amply justified by the results, and it is to be hoped that more may be brought to see the profit to be gained by

adopting scientific methods of work. The university man who has specialised in chemistry can assist the manufacturers in this by bringing to bear on the *rationale* of the technical processes the general scientific knowledge which he has gained during his college course, and his experience of methods of research and manipulation; he can thus materially benefit his employer by improving the quality of his products or enabling him to turn out his goods at a cheaper rate. Let the manufacturer, be he dyer, tanner, pulp-maker, or ironmaster, indicate only that he is willing to find employment for men educated in the higher branches of scientific work, and the universities of the Dominion will supply them. Where chemical processes are used, it is essential for the prosperity of this country that all the available scientific knowledge should be brought to bear on them, in order that they may continue to improve and to develop even more than they have done in the past decade. Canada, with its immense natural resources, and its water power should, in time and with proper management and assistance in the lines indicated, become one of the largest producers of the world's supplies.

In conclusion I wish to acknowledge the great assistance I have received from Mr. Fred. P. Clappison, B.A., Fellow in Political Science in the University of Toronto, in gathering together for me from all quarters, the information required for this short and imperfect account of the chemical industries of the Dominion. In particular his help in connection with the statistics contained in the text and in the appendices has been invaluable. To the gentlemen who so kindly answered our enquiries as to their particular industries and placed valuable material at our disposal, I desire also to convey my hearty thanks.

Appendix I.

The Iron Ores of Canada.

Nova Scotia.—Magnetites in enormous quantities at Nictaux, in Annapolis County, at Whyhogomah, in Inverness County. Specular and red haematite at Nictaux, Stewiacke, Pictou, Antigonish, Guysboro, East Bay, and many other points. Limonite, specular, spathic clay ironstone and haematite at Londonderry. Mineral fuel and

fluxes are in close proximity throughout the whole district.[77]

Cape Breton.—Extensive deposits of brown haematite, magnetite, and spathic ores lying adjacent to the great coalfields.[78]

New Brunswick.—Magnetite and bog ores. Coalfields at Grand Lake and hardwood throughout the Province.

Province of Quebec.—Very extensive deposits of bog and lake ores, extending from the Province of Ontario to Gaspé. Magnetite deposits especially good at Sherbrooke, Leeds, Sutton, St. Jerome, and in Pontiac County. Hardwood and limestone abundant. Deposits of chrome-ironstone found in 1895 in Coleraine. The "Eastern Townships" obtain iron by dredging in the Lac-a-la-Tortue. Magnetites at Hull, near Ottawa.[79]

Ontario.—Vast deposits from the Ottawa Valley to head of Lake Superior, comprising magnetite, red haematite, limonite, specular, and occasionally bog ores. The Helen Mine, at Michipicoten, is said to be one of the richest in the world. There are also extensive forests of hardwood, especially suited for the production of charcoal, and fluxes in abundance.[80]

Manitoba.—Magnetite, haematite, and bog ore on Lake Winnipeg. Hardwood in abundance.[81]

British Columbia.—Magnetic ores at Texada Island and Cherry Tree Bluff. Coal and wood in plenty. Collieries at Nanaimo (Naval coaling station for H.M.'s ships), Wellington, and Comox. A recent discovery of large deposits of magnetite has been reported in the Boundary Region, which at present mainly finds a use as a flux.[81]

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[77] Nova Scotia Report of Mines, 1901.
[78] Report of Geological Survey.
[79] Mines and Minerals of Quebec: Department of Mines.
[80] Bureau of Mines Report, Ontario, 1901.
[81] Geological Survey of Canada, 11th Annual Report.

Appendix II.

Metallic Production of Canada, 1892—1901.

Metals.	Value, 1892.	Value, 1897.	Value, 1901.	Value, 1902.
	Dols.	Tons.	Dols.	Dols.
Pig iron	637,421	53,796	1,212,113	..
		Dols.		
Steel slabs and billets	..	347,280	..	..
Copper in mattes	818,580 [82]	1,501,660 [82]	6,600,104 [83]	..
Nickel in mattes	1,399,176 [83]	1,399,179 [83]	4,594,523 [83]	..
Arsenic	1,000	..	41,676	50,000 [84]
Gold	907,601	6,190,000	24,462,222	12,500,000 [85]
Silver	193,441	2,613,173	2,993,668	..
Aluminium	..	..	1,000,000 [85]	1,643,250
Lead	49,422	1,396,853 [84]	2,190,787 [83]	..

[82] Value of metal, if refined.
[83] Value of matte.
[84] Estimated.
[85] Letter from Mr. B. E. Walker, General Manager The Canadian Bank of Commerce.

Appendix III.

Iron and Steel Production.

Company.	Plant at	Built.	Source of Ore.	Employees, 1902.	Output in Tons.				Capacity of Furnaces in Tons per Day.		Capitalisation.
					Pig Iron.			Steel.			
					1892.	1901.	1902.	1901.	1892.	1902.	
											Dols.
Canada Iron Furnace Co.	Midland, Ont.	1899	Ontario	.	..	18,948	..	..	..	..	1,000,000
	Radnor, Que.	..	Quebec	..	5,574	31,159	..	..	40	..	..
	Londonderry, N.S.	1887	N.S.	(86)	28,052	(86)	(86)	(86)	40,000 per ann.	150	..
Hamilton Steel and Iron Co.	Hamilton, Ont.	1896	Ontario and U.S.A.	1,000	(88)	51,701	..	9,473	(88)	180	1,500,000
Nova Scotia Steel and Iron Co.	New Glasgow, N.S.	..	N.S.	965	29,502	28,407	..	23,916	100	100 pig, 100 steel.	5,000,000
Desoronto Iron Co.	Desoronto, Ont.	..	U.S.A.	..	..	13,701	..	..	..	..	..
Dominion Steel and Coal Co.	Sydney, N.S.	1901	Newfoundland	6,000	(88)	27,643	191,259	86,424 (1902)	(88)	1,000 pig, 800 steel.	33,000,000
John MacDougall and Co.	Drummondville, Que.	..	Quebec	..	..	793	..	..	6	..	..
Cramp Ontario Steel Co.	Collingwood, Ont.	1900	Ontario and foreign.	(87)	..	..	..	..	..	200,000 per ann.	..
Lake Superior Power Co.	Saulte Ste. Marie.	1901	Ontario	500	(88)	(87)	(87)	(87)	(88)	..	117,000,000

(86) Not in operation, due to repairs being made. (87) Not in operation yet. (88) Not in operation.

Appendix IV.

Portland Cement and Plaster of Paris.

Firm or Company	Place.	Capital.	Capacity of Plant in Barrels per annum.	Output, 1902 (Barrels).	Date of Beginning Manufacturing
		Dols.			
Crescent Cement Co.	Longue Pointe, Que.	200,000	..	..	..
Canadian Portland Cement Co.	Deseronto, Ont.	1,500,000	250,000	250,000	1893
Lakefield "	Lakefield, Ont.	590,000	75,000	75,000	1902
Imperial "	Owen Sound, Ont. ...	250,000	50,000	50,000	1902
Grey and Bruce "	" " ...	100,000	30,000	20,000	1902
Owen Sound "	Shallow Lake, Ont. ..	199,000	100,000	100,000	..
Sun "	Owen Sound, Ont. ...	500,000	40,000	40,000	1902
National "	Durham, Ont.	1,000,000	300,000	..	1903
Hanover "	Hanover, Ont.	150,000	30,000	30,000	..
		4,399,000			
Albert Manufacturing Co. (Plaster of Paris)	Hillsboro', N.B.	350,000	..	60,000	..

Appendix V.

Carbohydrates.

Sugar from Beetroots.

Company.	Place.	Capital.	——	Output. 1902.	Capacity.
		Dols.			
Wiarton Beet Sugar Co.	Wiarton, Ont.	415,000	Began, 1901	..	350 tons of beet per day.
Ontario Sugar Co.	Berlin, Ont.	1,000,000	„	Over 6,000,000 lb. of granulated sugar.[89]	600 „ „
Dresden Sugar Co.	Dresden, Ont.	500,000	„	..	600 „ „
Wallaceburg Sugar Co.	Wallaceburg, Ont.	500,000	„	..	700 „ „
Knight Sugar Co.	Raymond, N.W.T.	1,000,000	Will begin 1903	..	400 „ „
			Sugar from Cane.		
Acadia Sugar Co.	Halifax, N.S.	..	..	..	..
Canada Sugar Co.	Montreal, Que.	..	..	..	..
St. Lawrence Sugar Co.	„ „ ...	750,000	..	100,000,000 lb. of raw sugar.	..

[89] Letter from Dr. A. F. Shuttleworth, 19.3.03.

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Canadian Section.

Meeting held at Toronto on Thursday, November 23, 1905.

DR. F. J. SMALE IN THE CHAIR.

CHEMICAL INDUSTRY IN BRITISH COLUMBIA.

BY PROF. W. R. LANG.

To consider fully all the industries visited last summer would occupy more time than can be allowed at this sitting. Much less would it be possible to do justice to the whole subject of the chemical industries in active operation in British Columbia on the strength of a comparatively short acquaintance with that province. An account of the mineral industries alone would occupy volumes, but it must be remembered that these are not the only ones: chemical works, sugar refineries, vinegar-making, and a host of other smaller industries are flourishing in the West, and a short and imperfect account of those visited will be found in the sequel.

In Victoria, Vancouver Island—the natural limit of one's Western travels—there is an excellent plant for the preparation of sulphuric acid. The lead-chamber process was in full swing, and a large experimental plant for preparing sulphur trioxide by the "contact" process was just in progress of demolition, to be set up again on the large scale. The manager expressed himself as perfectly satisfied with the results of their experiments, extending over a number of months, and looked forward to a successful working of the new process commercially. To hear that Canadian sulphur was not used in making the acid was somewhat of a surprise, but the inspection of a few figures

relative to the comparative cost of native sulphur imported by sailing ships from islands in the Pacific and the expense alone of bringing the sulphur—even if recovered from the sulphide ores there—from the Kootenay district, served to shatter at once the idea that all the materials necessary for the production of even this one substance could be obtained readily in the Dominion. In time, no doubt, importation of sulphur will be unnecessary, but at present the 500 odd miles of rail and water between Victoria and the Kootenay mines effectually prevent any use being made on the coast of the sulphur they might produce.

At the Parliament Buildings in Victoria, Mr. R. E. Gosnell kindly supplied literature and much information regarding the mineral industries of the province, an account of which will be given later on. Vancouver City contains two large breweries, a distillery, vinegar works, and a sugar refinery. This last is a very fine one, replete with all the most modern machinery, and producing both syrup and fine sugars, the raw materials from which are imported from Peru, Java, Fiji, and Central America. The vinegar works close at hand convert weak alcohol, obtained from the distillery, into vinegar by the "quick vinegar" process. The spirit is allowed to trickle through a series of large vats placed on three floors, one above the other, over suitably arranged shelves in the vats, to which a properly regulated air supply is admitted. The resulting vinegar is of a very good quality. Both distillery and vinegar works are the property of the same company. There are breweries also in Rossland and Nelson.

A couple of establishments in Victoria are engaged in the preparation of coffee and spices for the market, both of which are doing a fairly good business.

In Victoria is an extensive factory for laundry and toilet soaps, also paints, varnishes, and colours, and in Vancouver there are also soap works.

About the beginning of the present year, a Portland cement plant was erected, and put in operation on Vancouver Island, some distance from the city of Victoria. They have two rotary kilns in operation, though they expect to enlarge their plant in the near future. Fire bricks, drain-pipes, and tiles are also manufactured on Vancouver Island, and supply local demands; indeed, lime and brick are produced in almost every district. Fish canning might also be mentioned as a staple industry of the province.

British Columbia claims to be the "Mineral Province" of the Dominion: iron, gold, silver, lead, copper, zinc, mercury, and even platinum are being worked, while the coal deposits are a most valuable asset. The iron ores of British Columbia are practically the only ones of any importance along the northern coast of the Pacific, consequently iron manufactured there would have as a market all this territory. At present much of the iron used there comes by sea from Great Britain. Vancouver Island, the mainland, Kamloops, and, to some extent, East Kootenay are possessed of iron deposits. As cheap transportation of ores, coke, and fluxes are essential for the success of the iron industry, British Columbia is eminently fitted, with its coast and other waterways, to become a large producer. Vancouver Island has an abundant supply of coal of a good coking quality, while as to fluxes, the limestone found associated with the iron is exceptionally pure.

Circumstances have so far militated against the progress of this industry owing to the possible iron-master being unwilling to build blast-furnaces without a direct assurance from the mine-owners that they can supply his needs, and the mine-owners will not exploit their ores unless means of reducing them are promised. These difficulties seem now in a fair way of being removed.

A recent article in a Toronto newspaper, however, on the position and prospects of zinc in the province, states "... large shipments were made this year, but the producers are at a great loss through having to ship the ore to the United States or to Europe for treatment." This news must be encouraging to the province, as hitherto the occurrence of zinc in silver-lead deposits has been looked upon—and indeed penalised—by smelters as detracting from the value of the ore as a source of these two metals. In many cases, zinc was present in quantities necessitating separate treatment of the ore; this has evidently shown that zinc ores might with advantage be worked for that metal itself, as the market for spelter is increasing year by year.

The following is a short account of the working of the magnetic separator as applied to zinc ores as set forth in the official bulletin on mining, published by the British Columbia Government:—

"An important addition made last year to the concentrating plant of the Payne Mine, near Sandon, Slocan, was the magnetic separating plant for zinc ores. In the first

instance, a 42 per cent. blende concentrate is produced in the usual way by means of jigs and Wilfley tables. This is dried and then exposed to a moderate heat in a furnace of the revolving cylinder type, whereby the spathic iron (siderite) associated with the zinc is changed into a magnetic product. After cooling, the roasted product is sized in a set of vibrating screens and charged into magnetic separating machines of the Knowles type, thereby eliminating the magnetic iron and leaving the zinc blende as a 55 to 57 per cent. finished product. Some silver is contained in the blende, but after separation only a small percentage of iron and lead remains in the ore, thus making it a very desirable smelting material. The entire plant is automatic, and the cost of handling is therefore very small per ton. The Payne concentrator, in conjunction with which the separator is operated, produces a high-grade silver-lead product of an average value of about $100 per ton. It also possesses the material advantage of making a zinc product in the fourth compartment of the jigs."

The same writer also describes the use of oil—the Elmore oil process—for the treatment of the tailings remaining after the crushed ore has been subjected to the ordinary process of water concentration. The tailings are run on to two units of an Elmore oil plant. (One unit equals an estimated capacity of 25 tons per day.) These tailings are fed into mixing cylinders with water and oil from the storage tanks. These, of which there are three, are long iron cylinders, placed horizontally, and provided with inside baffle plates, which, as the cylinder is revolved at a low rate of speed by power, thoroughly mix the charge, bringing the oil into contact with every particle of material in the tailings. The oil has the property of catching up and retaining fine particles of sulphides and of free gold. From the mixers, the charge is flushed with water into settling tanks. Here the gangue matter settles to the bottom, while the oil, being lighter than the water, floats on the surface, retaining with it the metallic sulphides &c. The oil can, of course, only carry a limited amount of sulphides to an extent such as will not render the oil-mineral compound heavier than the water.

The tailings from the first mixer are passed through a second and a third mixer to catch any sulphides that have not been taken up by the oil in the earlier process. The mineral-charged oil is next run into a centrifugal oil

extractor, a machine 4 ft. in diameter, revolving at a speed of 1,000 revolutions per minute, and the oil concentrate that remains is carried to a second extractor, into which a steam jet is introduced, this removing more oil and to some extent drying the concentrate, which is thereafter sent to the smelter for final treatment.

Platinum and osmiridium have been found in small quantities in the black sands of the Cariboo district, but little has yet been done to save these metals. Mercury, in the form of cinnabar, has been found in the neighbourhood of Kamloops Lake, and the deposits were treated for the extraction of quicksilver for a number of years. Though in the meantime unsuccessful, there is a strong probability of these mercury ores being profitably treated at no distant date.

Attracted by the reputation that West Kootenay has for its smelting and reduction works, an eastward trip was made as far as Revelstoke, and thence by C.P.R. steamer down the Arrow Lakes to Trail and Rossland. At Trail are situated the largest lead-copper reduction works in Canada, now known as the Canadian Smelting Works, and owned by the C.P.R. The buildings and appliances of different kinds cover some 45 acres, and electric power is obtained from the Kootenay Power Company's Station at Bonnington Falls; there is a total of 1,000 horse power in motors. The ores treated are varied in character, and are custom ores entirely. The Rossland mines supply most of the copper-gold ores, which, after crushing and sampling, are carefully assayed. Most of the ore is roasted in heaps of from two to three thousand tons each, which process occupies from four to six weeks. No attempt is made to save the sulphur, which is allowed to burn off. This is due to the lack of a convenient market and to other causes. With more branch lines of railway, systems of water transport, and demands for sulphur, consequent on the increase of population, and the resulting building of towns and cities throughout the West, will come the utilisation of this valuable element for the numerous industries that this and the next generation will see being carried on in the province. In the meantime, the sulphur content of the ores must continue to be waste material. The roasted ores are fed mechanically to the furnaces, and the first matte produced contains 14 to 15 per cent. of copper. It is roasted, granulated, and briquetted, and re-smelted with some raw ore, yielding a high grade matte

of about 55 per cent. copper. This last is treated elsewhere, and brought up to 98 per cent. of copper, when it is sent to Eastern refineries, where the gold and silver are extracted by electrolytic methods.

An interesting feature of the Trail Works is the production of electrolytic lead by the Betts process; this is the first instance of this process being carried out on the commercial scale. A plant for making lead pipe up to 4 in. in diameter is included in the company's equipment, the first of its kind in Canada for producing lead pipe from Canadian lead. It should also be added that this is the first company to make silver bullion in quantity from Canadian ores smelted on the spot. The establishment of works in Eastern Canada for the corrosion of lead, and the manufacture therefrom of white-lead and other pigments, should open up a large market for the output of this metal from British Columbia. As an example of a really fine chemical industry, the works at Trail holds a high position. Large roomy laboratories, store-rooms, and assay furnaces—not to mention the works proper—are a fitting preparation for a visit to villa residences and tennis courts on the high banks of the river, which the Company has erected for its officers.

Lack of time prevented a visit being made to Grand Forks, where are installed Bessemer converters, having a capacity for treating about a hundred tons of copper matte daily—an exceedingly large amount. There blister copper of about 99 per cent. purity is turned out in cakes of about 100 lb. each.

A short railway journey from Trail brings one to the picturesque town of Nelson, situated on the hill-side above the west arm of Kootenay Lake. Here the Hall Mining and Smelting Company erected their works on the high ground above the town about 10 years ago, principally for the treatment of ores from the Silver King Mine on Toad Mountain, which is connected with the works by an aerial line. Since 1900, the Company has smelted custom ores as well, mainly lead ores, very little being done with the copper-silver ore from the Silver King Mine. The blast furnaces have a capacity of from 180 to 200 tons of lead charge per day; the slag is automatically removed by water granulation, the matte crushed, rolled, screened, and roasted. The roasted matte is briquetted and conveyed to the blast furnaces.

Fifty-five miles by water from Nelson is Kootenay

Landing, the present western terminus of the Crow's Nest Pass Route, the construction of which through the mountains of East Kootenay and across the plains of Southern Alberta to Lethbridge—a distance of 289 miles—occupied less than fifteen months! Truly, a magnificent piece of work. In six hours or so from this terminus, the great coal belt of East Kootenay is first encountered, which is supposed to be the largest undeveloped coal measures in the world.

It would be beyond the scope of this short account of a chemist's wanderings in British Columbia to enter into any historical or statistical particulars of the opening up and development of these coalfields: the chemist is more interested in the proper utilisation of the coal, of the products of its distillation and of the coke resulting therefrom. The physical conditions at Coal Creek and Morrissey are such that a departure from methods prevailing at most collieries where coke is made has been necessary, for owing to there not being room in the valleys near the mines for a sufficient number of coke ovens, these have had to be built away from the mines. The ovens of the Coal Creek Colliery are at Fernie, between four and five miles from the mines; the Morrissey ovens are nearly two miles from the mines. The slack coal for coking in these ovens is loaded directly on to railway dump cars, and hauled to storage bins built near the ovens. At Michel, the slack is collected from the screens in pockets, conveyed to an elevator, discharged on a second conveyor, and distributed to bunkers as required.

The coke ovens are of beehive shape, diameter 12 ft., and have a circular "eye-hole" or chimney at the top. They are built in double rows, of fire-brick, with supporting walls and piers of stone masonry, filled in between with fireclay. A single standard-gauge railway track runs along the top of each battery, and on this are hauled, by light steam locomotives, the side-discharge steel lorry cars, which charge the ovens with 6½ tons of slack each. The production of coke per charge is from 3·90 to 4·22 tons, the average being 1 ton of coke from 1·6 tons of coal. The time for burning is 60 to 72 hours, which gives a daily production per oven at the rate of 1·3 to 1·6 tons. No provision is made to recover the by-products. The coke is "quenched" or cooled, and the dirt washed off by hose-watering inside the ovens. The coke is generally long, lustrous, and firm, containing up to 94 per cent. fixed

carbon, 4·50 per cent. ash, and 0·75 per cent. sulphur.* The ovens at Fernie, Morrissey, and Michel number well over 1000.

The Government Bulletin on Mining, 1904, also gives the following particulars regarding cost, &c. :—Coke is supplied at $4.25 to $4.50, f.o.b., and freight to boundary points is $2 to $2.25, so about $6.50 per ton is the cost delivered at the boundary smelters. Coal from Vancouver Island Collieries used to cost $10, and coke $11, delivered at Nelson ; now coal from the Crow's Nest Pass Collieries is delivered there at about $5, and coke at about $6 ; so the beneficial influence of the Crow's Nest Pass Coalfields has here been unmistakably demonstrated by a reduction in cost of fuel of nearly 50 per cent.

Two railways give the Crow's Nest Pass Coalfields access to markets for their coal and coke. The Canadian Pacific Railway Company's Crow's Nest line leaves its present main line at Dunmore Junction, Assiniboia, reaches Michel at 224 miles, Fernie at 247 miles, Morrissey Junction at 256 miles, and Kootenay Landing at 394 miles. From Kootenay Landing to Nelson the distance is 52 miles, of which distance 32 miles, to Proctor, is by water, the freight cars being transferred on large scows or barges, each carrying 10 cars. Smelting points in British Columbia reached by Canadian Pacific Railway are distant from Fernie as follows :—Nelson, West Kootenay, 199 miles; Trail, West Kootenay, 251 miles ; Grand Forks, Boundary, 299 miles ; Greenwood, Boundary, 318 miles ; Boundary Falls, Boundary, 321 miles.

At the coke-ovens here the volatile products of the distillation of the coal share the same fate as the sulphur at the smelters, and possibly for the reasons suggested when considering that question. The following figures, calculated from the *data* regarding output of coke during 1903, proportional yield of coke to coal used, and average analyses of coals (to be found in Official Bulletin, No. 19, of the British Columbia Government, 1904, pp. 117 and 119), give some idea of the amount of useful material in the form of coal-tar and ammonia that was lost that year :— 167,700 short tons of coke were produced from 268,320 tons of coal (1 ton of coke from 1·6 tons of coal). The difference, 100,620 tons, represents gas, tar, and liquor ;

* Official Bulletin, No. 19, Mining in British Columbia, 1904, p. 117.

the amount of coal-tar obtained would be, approximately, 10,000 tons, or 1,780,000 galls., worth $53,400 (at 3c. per gall.), and the ammoniacal liquor, 21,000 tons (4,200,000 galls.), worth $42,000 if its value were 1c. per gall. This gives a total value of $95,400.

These figures speak for themselves. The present demand for the distillation products of coal-tar and for ammonia has not as yet justified the saving of these substances. No doubt when the Canadian Pacific Railway continues its Crow's Nest line to the coast, and as other industries spring up in British Columbia and in Alberta, a market will be found for their disposal. As was stated in an article on the Chemical Industries of the Dominion, published in the "Transactions of the Canadian Mining Institute," 1904, the Dominion Iron and Steel Company at Sydney, C.B., now utilises all the coal-tar produced from their coke-ovens for making benzol, creosote oil, and carbolic acid. The demands for their products in Canada are not sufficient, however, so a considerable amount is exported to Europe and the United States. The positions of Fernie and Sydney are, perhaps, hardly comparable as regard transport facilities, but no doubt a day will come when the ninety-five thousand odd dollars at present being dissipated at the former place will be saved, and advantageously treated or disposed of.

THE COMPOSITION AND TENSIONS OF DISSOCIATION OF THE AMMONIACAL CHLORIDES OF CADMIUM.

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BY

WILLIAM ROBERT LANG, D.Sc.,

AND

ALBERT RIGAUT.

From the Transactions of the Chemical Society, 1899.

The Composition and Tensions of Dissociation of the Ammoniacal Chlorides of Cadmium.

By William Robert Lang, D.Sc., and Albert Rigaut.

The phenomena of dissociation were first investigated by H. St. Claire Deville and by Debray (*Compt. rend.*, 1867, 64, 603; 1868, 66, 134). Following on this, Isambert (*Ann. de l'École Normale*, 1868) carried out an exhaustive research on the tensions of dissociation of certain ammoniacal compounds of the metals, and, by applying the principles set forth in Debray's papers, was enabled to arrive at the true composition of these compounds. He shows that a definite chemical compound always has a constant tension of dissociation. Quite recently, Jarry (*Thèse de la Faculté des Sciences de Paris*, 1899) has applied the laws of dissociation in investigating ammoniacal compounds obtained with a solution of ammonia, and has established the fact that, for the ammoniacal halogen compounds of silver, formation and decomposition stop when the liquid saturating the compound is under a pressure equal to the tension of dissociation of the substance in vacuum. We have studied, from this point of view, the compounds formed between ammonia and cadmium chloride, using ammonia in the gaseous condition, in the liquid form, and in solution.

By the action of gaseous ammonia on dry cadmium chloride, Croft

(*Phil. Mag.*, [iii], 21, 355) obtained a dry powder, much heat being developed at the same time, and the mass increasing in bulk. To this compound he gave the formula $CdCl_2,6NH_3$. He also employed a solution of ammonia, and prepared a granular, crystalline substance corresponding with the formula $CdCl_2,2NH_3$. André (*Compt. rend.*, 1887, 114, 908) also, employing a solution at 0°, formed a compound to which, as the result of one experiment, he gave the formula $CdCl_2,5NH_3$. We have followed the method of preparation indicated by him, and find that this compound is identical with that obtained by Croft.

Our procedure was as follows: three to four grams of cadmium chloride, rendered anhydrous by heating almost to the point of fusion, were placed in a tube with the neck drawn out, to allow of its being afterwards sealed at the blowpipe, and the whole immersed in solid carbonic anhydride. Dry gaseous ammonia was passed slowly into the tube, when the chloride increased in bulk largely, and, in about 2 hours, a layer of liquid ammonia had formed on the surface of the solid compound; the tube was sealed and left for 20 hours. It was found preferable to use the salt in small lumps, as, when in powder, the liquid failed to penetrate through the mass, even on standing for a month. The tube was then cooled to $-70°$ and opened, the temperature cautiously raised to $-30°$ by means of methylic chloride, and the liquid ammonia expelled. In some of our experiments we allowed the ammonia to evaporate at 0°. After this the tube was sealed at the blowpipe and weighed. Analysis gave:

	Calculated for $CdCl_2,6NH_3$.	Found.
$CdCl_2$	64·21	64·02
NH_3	35·8	36·00

After reopening and heating at 100° until no more ammonia was evolved, analysis gave, as the result of several determinations:

	Calculated for $CdCl_2,2NH_3$.	Found.
$CdCl_2$	84·4	84·49
NH_3	15·6	15·51

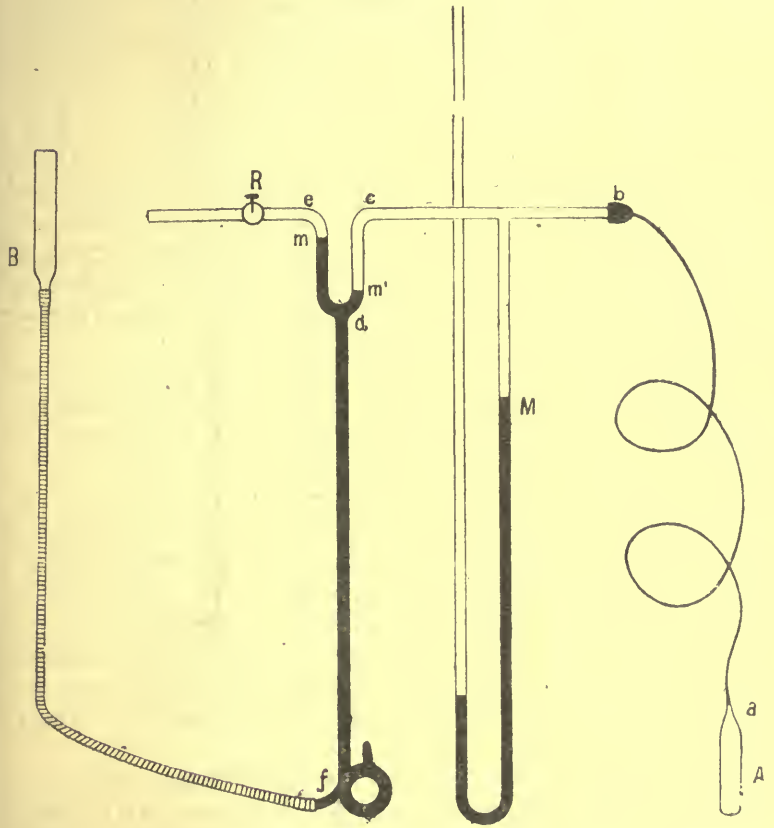
The formula of this compound is therefore $CdCl_2,2NH_3$; it is inodorous, and, like the corresponding salt of zinc, only begins to decompose at about 210°. At 360°, decomposition is still incomplete, and when raised to close on 400° it fuses, giving only a *trace* of oxychloride and of chloride of ammonium.

In order to determine the tensions of dissociation of this hexammoniacal cadmium chloride, we used an apparatus similar to that of Jarry, and which is shown in Fig. 1.

A glass vessel, *A a*, containing the substances under consideration,

and in which the compound was prepared, is fixed by means of sealing wax to one of the extremities of a length of narrow lead tubing. The use of rubber should be avoided when working with gaseous ammonia, as the latter is readily dissolved by the rubber, and is given off again when the pressure is diminished. This tube is attached at *b* to the apparatus, which is mounted on a solid stand. The glass tube *b c d e* allows of communication being made with a mercury pump by means

FIG. 1.



of the stopcock *R*; the small U-tube *c d e* communicates by means of the vertical tube *d f* with *B*, which contains mercury, and which can be lowered or raised at will. This allows of the tube *c d e* being filled with mercury, and so shutting off the vessel *A*, when a vacuum is produced, from the stopcock *R*. This is a very necessary precaution, as the gaseous ammonia dissolves in the grease with which this stopcock is lubricated. vacuum is maintained in the tube *m*, the

difference of levels at m and m measures directly the pressure in A. As the tube $m\ m'$ is only some 30 cm. high, higher pressure can be read on the tube M, which is open to the air, and stands about 2 metres high.

The numbers we obtained are:

Temp.	Press.	Temp.	Press.
0°	46 mm.	50°	455 mm.
13	68	52	511
22	133	59	631
25	152	60	696
31	181	61	711
39	235	63	776
44	290	65	831
48	411	69	931

The readings were made in the following manner: The temperature of the water-bath in which the vessel A was immersed was very gradually raised, and the lamp removed; the thermometer fell slowly, and the mercury in the manometer rose, and, when it appeared to have attained a maximum, the readings were taken, at the same instant the temperature in the water-bath being noted.

It will be seen that above 62° the substance $CdCl_2,6NH_3$ can no longer exist, whilst we have at 100° a very stable compound, $CdCl_2,2NH_3$. It must therefore be at temperatures between 62° and 100° that the intermediate products are obtained.

We prepared this ammoniacal compound in the wet way also. By moistening hydrated cadmium chloride with a 20 per cent. solution of ammonia until thoroughly saturated, the compound is formed, increase in bulk taking place and much heat being developed. The crystals so obtained were dried over lime, and found to correspond with the formula $CdCl_2,2NH_3$. If a solution of cadmium chloride in aqueous ammonia is evaporated over lime, or if the crystals formed when this solution is heated to 50° are collected, the same compound is in every case obtained.

In order to obtain a compound containing more than 2 molecules of NH_3 by means of aqueous ammonia, it is necessary to pass a current of gaseous ammonia into a solution of cadmium chloride in a 20 per cent. solution of ammonia, keeping the temperature at 0°. An abundant precipitate is thus got of small, transparent crystals, which, when dried and pressed between filter paper, become opaque, losing ammonia. André (*loc. cit.*) also prepared those crystals, and, as mentioned elsewhere, gave them the formula $CdCl_2,5NH_3$. From an analysis of them, we are led to the conclusion that the formula is not $CdCl_2,5NH_3$, but that it is as indicated by

Croft (*loc. cit.*), namely, $CdCl_2,6NH_3$. This confirms Jarry's conclusions regarding the ammoniacal compounds of silver (*loc. cit.*). We have, besides, determined the tension of dissociation of this compound. At 22°, we found it to have a tension of 147 mm. instead of 135 mm. The excess obtained from this product is due to a small quantity of vapour of water, difficult to completely remove by pressing with bibulous paper.

From these experiments, it appears to us that it is possible to obtain the same ammoniacal compounds, either by the use of gaseous ammonia or from a sufficiently concentrated solution.

A short note, containing a portion of the results here set forth, has been communicated to the Académie des Sciences, Paris, by Prof. Troost, of The Sorbonne, to whom we desire to tender our best thanks for his kind assistance and advice.

CHEMISTRY DEPARTMENT,
UNIVERSITY OF GLASGOW,
August, 1899.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY

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WILLIAM R. LANG, B.Sc., F.C.S.,

ON

I.—ALFRED NOBEL AND THE DEVELOPMENT OF THE MODERN HIGH EXPLOSIVE.

II.—THE SECONDARY PRODUCTS OF THE COMBUSTION OF GUNPOWDER.

GLASGOW:

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Alfred Nobel and the Development of the Modern High Explosive.

By W. R. Lang, B.Sc., F.C.S., Chemistry Department, University of Glasgow.

(Containing the results of the author's investigations into the secondary products of the combustion of gunpowder.)

[Read before the Society, 8th March, 1899.]

Part I.

Alfred Bernard Nobel was born at Stockholm, in Sweden, on 21st October, 1833, and at the time of his death, in December of 1896, his name was familiar to all interested in the subject of explosives.

With the largest and most complete factory in the world at our very door, so to speak—I refer to the Ardeer works—it would be strange if we in Glasgow were not specially interested both in the man and in the gradual development of the modern explosive. At each stage in the progress made towards perfecting explosives we find Nobel in the forefront, and, before proceeding to discuss the subject, I propose giving a short *resumé* of his life and work. His father was a naval constructor, but was also interested in the making of mines and of torpedoes; indeed, for some years he worked in St. Petersburg under the Russian Government, but finally returned to Stockholm. Alfred, the third of four sons, was physically weak, and in his youth suffered from some spinal complaint, which necessitated great care in his early upbringing. When of sufficient age he was apprenticed to his father, and received in his works a thorough training as an engineer, thereafter proceeding to America, where he remained three years. Like his father, his chief hobby was explosives, and on the discovery of gun-cotton by Schoenbein in 1845, and of nitro-glycerine by Sobrero in 1847, they prepared those substances themselves, and Nobel senior tried them for his torpedoes and land mines. Till 1862 they continued experimenting chiefly upon nitro-glycerine, and in that year the necessary capital was found—not without considerable difficulty—and the first works for its manufacture started near Stockholm. Not long after this old Emanuel Nobel died, and the work was con-

tinued by his son. The production of nitro-glycerine experienced many vicissitudes, however, and, owing to the Stockholm works being blown up, the authorities refused to allow of its manufacture being carried on near the city. Not to be beaten, however, Nobel removed his plant to a barge anchored in Lake Mälaren, and there continued his experiments. Nitro-glycerine now began to attract considerable attention, and was used for many operations where hitherto gunpowder had been employed. Being a liquid—I shall consider the substance itself later—it could permeate any fissure or bore-hole into which it was poured, but this very property rendered it extremely dangerous and difficult to transport. To obviate this Nobel tried various absorbent materials, among them gunpowder, but, despite this, accidents continued to happen, and it looked almost as if Nobel's blasting oil would prove a veritable Frankenstein. Its creator found the remedy—a siliceous earth, known as kieselgühr, was used as an absorbent, and the resulting brown, pasty substance was given to the world in 1866 under the name of "Dynamite." Being comparatively safe to handle, this new substance soon came extensively into use, and Nobel succeeded in introducing it into America, where a company was formed in 1868, and works started for its production in San Francisco.

The success which met the employment of both gun-cotton and dynamite during the Franco-German war brought these new and powerful explosives to the front, and at the end of the war its manufacture was commenced in France. Shortly afterwards Nobel's Explosive Company, Limited, came into existence, and the works at Ardeer were started, which has now become the largest and most important factory in the world.

The principle underlying all explosive action is the sudden formation of a large volume of gaseous matter which, at the temperature of the explosion, becomes greatly expanded, and in its effort to assume its natural volume a propulsive, rending, or shattering action is the result. In order to get its full effect, confinement of some sort is necessary, and it is found that the rate of propagation of an explosive reaction varies with the pressure under which it may be. Gunpowder will simply burn without exploding if fired in an unconfined space; some external pressure is required to render its decomposition at all violent. Other more

energetic explosives, such as nitro-glycerine, can effect their purpose with no other pressure or confinement than that of the atmosphere; the action in this case is so sudden that the air has not time to be moved even, and has the same effect as what is known as "tamping."

For convenience we may divide explosives into two classes—*explosive mixtures* and *explosive compounds*. These, in turn, may be further subdivided according to the nature or action of their several ingredients. By an *explosive mixture* is understood a mechanical mixture of some combustible body and some other substance or substances which contain in them, in an available form, the supporter of combustion, viz., oxygen. Chlorate of potash, nitrate of potash, and other highly oxygenated bodies are the usual ones used, and may be likened to magazines of condensed oxygen, ready to give up their contents at once when induced to do so by the occurrence of the necessary conditions of temperature, etc. An *explosive compound*, on the other hand, contains the combustible and the supporter of combustion, so to speak, already within itself, all combined together to form a molecule. The elements of which this latter class is composed are oxygen, hydrogen, nitrogen, and carbon, and are united together, forming a definite compound in a very unstable condition of chemical equilibrium, and which readily becomes decomposed by a very slight disturbing cause. The action in this case is extremely rapid, and to this class belongs what we may call the "modern high explosive."

The most important *explosive mixture* is gunpowder, in which we have carbon and sulphur, the combustible bodies, and potassium nitrate (saltpetre), the source of oxygen. This salt retains its oxygen firmly in combination, and before it will part with it some very considerable disturbing cause is necessary. Hence in gunpowder we have a perfectly safe substance, as neither friction nor percussion will cause an interaction between its constituents.

I do not purpose entering into a description of the manufacture of gunpowder, but wish to consider the theoretical and practical effect of its explosion. In some explosive mixtures chlorate of potassium is substituted for nitre as the source of oxygen, but they are found to be too shattering in their action. They are much more sensitive to friction and percussion, the oxygen being held in combination with less tenacity than it is in potassium nitrate. In estimating the explosive force generated by any gunpowder,

the percentage of available oxygen in the nitre or chlorate is not the only factor to be considered. The investigations of M. Berthelot in the domain of thermo-chemistry have shown that the heat of formation of these salts plays an important part.

The ingredients of ordinary gunpowder are mixed in varying proportion, but the average composition may be taken as—

KNO_3, - - - - -	75 parts
S, - - - - - -	10 ,,
C, - - - - - -	15 ,,
	100 ,,

(The rifle powders adopted by the governments of the world differ but slightly from this.) These are thoroughly incorporated with water, and after pressing, drying, and granulating, it is ready for use. A powder suitable for small arms will not do, however, for guns of larger calibre. If we consider for a moment the difference between the weight of the projectile in an ordinary rifle and that in a piece of heavy ordnance, and the comparative power of resistance of the gun itself, we see that the rate of combustion must of necessity be regulated in order to overcome the inertia of the projectile gradually, and prevent a sudden rupture of the breech. At the same time, the maximum *muzzle velocity* must be aimed at. In order to regulate the combustion, therefore—which is the same thing as controlling the amount of gas evolved at the first instant of inflammation—the size and form of grain must be considered. Theoretically, what we should endeavour to do is to present a comparatively small surface at the *instant* of ignition, and gradually increase this towards the final stage of the reaction, after the inertia of the projectile has been overcome. To do this, various sizes and shapes of powders are employed, and, roughly speaking, it may be said that the larger the piece of ordnance the larger the size of grain required. *Mammoth powder*, *cubical*, *pellet*, *hexagonal*, *prismatic*, *pebble*, and others, are those mostly manufactured, and not only do their shapes and sizes differ, but, from what has been already said, it will be understood that the rapidity of combustion is also affected by the *density* of the grain.

Coming now to the chemical changes which occur during an explosion of gunpowder, the most simple way of expressing the reaction is—

$$(a)\quad 2KNO_3 + 3C + S = K_2S + 3CO_2 + N_2\,;$$

but this, as has been shown by the investigations of, among others, Sir Frederick Abel, does not by any means indicate the complete reaction. Many solid products besides potassium sulphide are formed, sometimes unburnt carbon and sulphur; and, after much investigation, Nobel and Abel have come to the conclusion that "the metamorphoses of gunpowder *cannot* be represented by an equation." Under different conditions they obtained from the same sample different products. Without entering too fully into the theories put forward, the results of many investigations point to the following explanation of what takes place. At the moment of initial explosion—and this will be the case in the bursting of a shell—the reaction may be represented thus---

$$(b)\ 16KNO_3 + 13C + 5S = 3K_2CO_3 + 5K_2SO_4 + 9CO_2 + CO + 8N_2;$$

but in the bore of a gun these products of combustion remain at a red heat in contact with—though for a *very* small space of time —free sulphur and carbon, with the result that reactions occur, causing the formation of potassium sulphide and more carbonic anhydride, which latter aids in the expulsion of the bullet from the barrel. The reactions may be represented by the equation—

$$(c)\ 4K_2CO_3 + 7S = K_2SO_4 + 3K_2S_2 + 4CO_2.$$
$$(d)\ 4K_2SO_4 + 7C = 2K_2CO_3 + 2K_2S_2 + 5CO_2.$$

The presence in nearly all ordinary gunpowder of more sulphur and carbon than is required by equation (*b*) serves to explain these last reactions.

With a view to ascertaining the correctness of this theory—more particularly of the last two equations—I am at present, and have been for some little time, investigating the subject, and the results arrived at will be found at the end of this paper.

The study and perfecting of the other great class of explosives, namely, *explosive compounds*, was the life-work of Alfred Nobel. A consideration of gunpowder as a type of the *mixture* class was necessary before proceeding further, as many of the modern explosives in use are mixtures of the two classes.

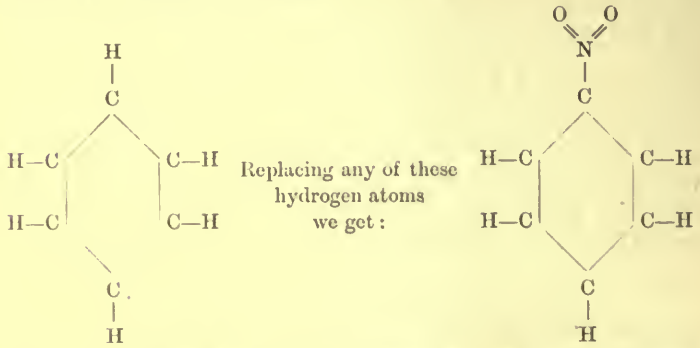
Explosive *compounds* are prepared from various organic substances containing carbon, hydrogen, and oxygen, by the action upon them of nitric acid. They are commonly spoken of as *nitro*-compounds, though, correctly speaking, only a very few of

them belong to this class, but are *ethereal salts* or *esters.* A knowledge of the formation of the true *nitro-compounds* will materially assist us in understanding the production of the *esters.* Hydro-carbons of the aromatic or benzene series are the most readily subject to the action of nitric acid, and the effect of this substance can best be represented in equation form—

$$C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O.$$

Benzene + nitric acid = nitro-benzene + water.

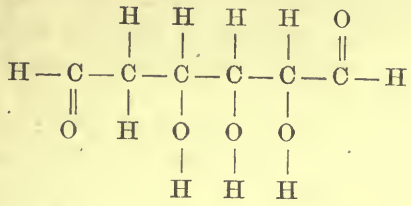
One atom of hydrogen in the benzene has been replaced by the radicle (NO_2), and this can be better understood if we use the structural formula for benzene:—



One, two, or three atoms of hydrogen can readily be replaced, giving mono-di- or tri-nitrobenzene. Similarly, other organic radicles may replace H in benzene, so by the introduction of the radicle (OH) "hydroxyl" we get the compound C_6H_5 (OH) phenol, or common carbolic acid. The presence of the hydroxyl group does not prevent the further introduction of the (NO_2) group, and by acting on this substance with nitric acid we get (as before, a mono-, di- or) tri-nitro-phenol, which is more usually known as *picric acid*, a powerfully explosive substance. Heat alone does not cause picric acid to explode, it merely burns quickly, but it can be *detonated* by an ordinary fulminate cap, or even a sharp blow on an anvil will cause its sudden decomposition. Some powders have been manufactured containing this substance, but we need not consider them here.

Similar to the nitro-compounds, though, as has been already pointed out, not exactly analogous, is *gun-cotton.* In the '40's

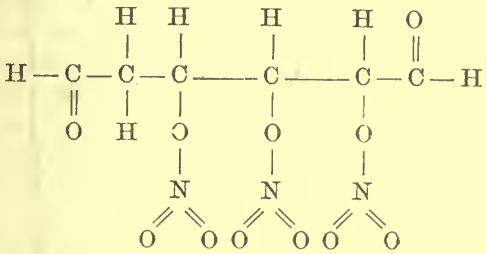
several experimenters were trying the effects of nitric acid on starch, woody fibres, and other bodies of the kind, but to Schœnbein belongs the credit of having produced nitro-cellulose, and realised the importance of his discovery. Cellulose (cotton wool, &c.) has the empirical formula $C_6H_{10}O_5$, which, regarding it as an alcohol, *may* be written $C_6H_7O_2(OH)_3$; or graphically—



By proper treatment with nitric acid the three *hydrogens* of the hydroxyl groups are replaced by the nitryl radicle (NO_2) thus—

$$C_6H_7O_2(OH)_3 + 3HNO_3 = C_6H_7O_2(O.NO_2)_3 + 3H_2O,$$

or graphically—



forming *tri-nitro cellulose* or *gun-cotton.*

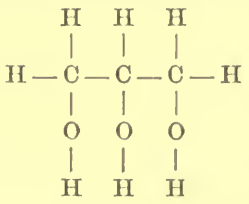
In the process of manufacture the cotton, after being thoroughly purified, is dipped in a mixture of concentrated nitric and sulphuric acids—the latter serves to absorb the water produced during the reaction and so prevent the undue dilution of the nitric acid. Absolute purity of both the cotton and reagents, and the complete removal of all traces of these acids by subsequent washings, are essential to the safety of the resulting nitro-cellulose; and Von Tenk, who investigated the matter very fully, has indicated the chief points to note, and the precautions to be observed in order that the gun-cotton may not be dangerous to keep or handle. For use, gun-cotton is pressed into cakes or slabs

and is now one of the most useful, convenient, and safe explosives that we have. It may be carried about *wet*, and even in that condition can be exploded by the proper means. When dry it is inflammable, but unless the mass is very large, may be set on fire with perfect safety, and will simply burn away quietly as would cotton in its un-nitrated condition. In appearance it resembles the material from which it is made, and this in the early stages of its history led to considerable doubt being expressed as to its being a definite compound at all, and not merely cotton *saturated with* the liquids employed.

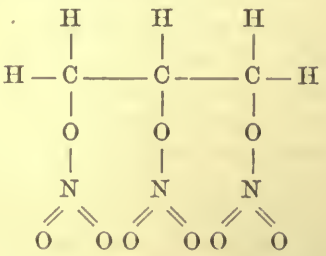
These doubts as to gun-cotton being a definite chemical compound caused considerable discussion, and Sobrero, a pupil of the celebrated French chemist Pelouze, decided to try the effect of nitric acid on glycerine, a substance analogous to cotton in composition. Being a liquid it was considered highly improbable that it would be capable of *absorbing* another liquid like nitric acid and retaining it merely in its pores. This was tried, and a compound was produced which announced its presence by a violent explosion happily unattended by any serious accident. Nobel soon came to hear of this, and at once entered heart and soul into an investigation of its properties, and about 1862 invented a process for its rapid manufacture, patenting the same under the name of *detonating oil*. In order to prepare nitro-glycerine a mixture of strong nitric acid and sulphuric acid are brought in contact with glycerine, when a reaction represented by the following equation takes place :—

$$C_3H_5(OH)_3 + 3HNO_3 = C_3H_5(O.NO_2)_3 + 3H_2O$$
glycerine = "nitro-glycerine."

Its molecular structure may be represented thus :—



Glycerine.



Nitro-Glycerine.

Like gun-cotton, as will be seen by comparing this formula with that of nitro-benzene and picric acid, nitro-glycerine is not in the proper sense of the term a *nitro-compound*, but rather a *tri-nitrate* of the radical *glycerl*. It would be pedantic, not to say impossible, to attempt to alter its accepted designation, but it is as well to understand thoroughly what its true structural composition really is.

The manufacture was carried on both in Europe, by Nobel, and also in the United States, and the accidents attending its preparation were frequent and disastrous. Improvements in the methods of mixing the liquids were introduced, and notably the employment of compressed air in forcing the glycerine into the acid mixture, as done by Nobel, proved a factor in minimising the danger attending the reaction. The glycerine was blown into the mixture from below in a fine spray which caused each *particle* to be immediately subjected to the action of the acids, and, at the same time, occasioned a fall in the temperature. About 30° C. is the maximum temperature at which the reaction may be allowed to proceed with safety, though decomposition does not usually occur below 50° C. Careful watching is necessary to prevent an undue rise of temperature, and, should this happen, the mixture must be instantly "drowned" to prevent probable disaster. The nitro-glycerine formed is of different density than the waste acids, and, being insoluble, separates from them readily, when it is subjected to thorough washing to remove every trace of acid which, were it allowed to remain, would affect the product very materially, rendering it unsafe. Nitro-glycerine is poisonous, and produces nausea and faintness either when inhaled or if brought directly in contact with the delicate membranes of the nose or mouth. People of a highly nervous temperament are most readily attacked, and it says much for the enthusiasm of Nobel, who was nervous and sensitive in the extreme, that he persevered so in his investigations, when it is known how severely he must have suffered from the toxic effects of this compound. Nitro-glycerine, when pure, freezes at a point a little below 0° C., and, when once frozen, its thawing is a matter of no inconsiderable difficulty and danger.

The firing of nitro-glycerine is usually performed by a detonator. When pure it is not by any means so sensitive to friction as is

usually believed; if "pinched" between metallic surfaces, explosion occurs at once, but it has been dropped on to the ground from a great height, and the impact failed to explode it. The products of its decomposition—in whatever way this may be initiated—are given in the following equation:—

$$2C_3H_5(O.NO_2)_3 = 6CO_2 + 5H_2O + 6N + O.$$

(It will be seen from this that there is actually more oxygen contained in itself than is required for the complete combustion of the carbon and hydrogen), and from the above equation it is a simple matter to determine the amount of gas liberated; for each 227 gms. (the molecular weight) there will be produced, at standard temperature and pressure, 161·82 litres, and if this be measured at the temperature of the explosion, it will occupy 3,314 litres. This, at constant volume, will exert a pressure of 23,360 atmospheres.

Despite the many useful applications of nitro-glycerine, its employment was fraught with so many dangers—its carriage and handling also was a troublesome matter—that Nobel set himself to overcome these difficulties by mixing it with various materials. Gunpowder was tried, and even liquids in themselves not explosive, and which were removed before use, but all of no avail, and the employment of his "blasting-oil" was finally prohibited in many countries. By this time, however, Nobel solved the problem by absorbing the nitro-glycerine in a fine porous siliceous earth, *Kieselgühr*, producing a pasty brown mass, to which he gave the name *dynamite*. Dynamite proved to be safe to handle, impervious to shock, and could only be exploded by a powerful detonator, properly inserted in it, with an attached fuse. This new substance is described by himself in his patent specification as follows:—"This invention relates to the use of nitro-glycerine in an altered condition, which renders it far more practical and safe for use. This altered condition of the nitro-glycerine is effected by causing it to be absorbed by porous inexplosive substances, such as charcoal, silica, paper, or similar materials, whereby it is converted into a powder, which I call *dynamite* or *Nobel's Safety Powder*."

The shock of the explosion of these compounds—taking the one presently under our consideration as an example—is much too sudden where, as in quarrying, a slow rending action is desired, and, as the energy of the dynamite employed depended on the

amount of nitro-glycerine contained in it, some modifications were next tried. This brings us to the consideration of nitro-glycerine mixtures containing an active or an inactive base. *Dynamite* itself illustrates the latter class, while the following selection will serve to show the many varieties of the former class that are at present in use :—

"Giant Powder."—No. 1.

Nitro-glycerine,	75·0 parts.
Kieselgühr,	24·5 ,,
Sodium carbonate,	·5 ,,

"Giant Powder."—No. 2.

Nitro-glycerine,	40 parts.
Sodium nitrate,	40 ,,
Sulphur,	6 ,,
Powdered resin,	8 ,,
Kieselgühr,	8 ,,

"Atlas Powder."

Nitro-glycerine,	75 parts.
Sodium nitrate,	2 ,,
Magnesium carbonate,	2 ,,
Wood fibre,	21 ,,

"Vulcan Powder."

Nitro-glycerine,	30·0 parts.
Sodium nitrate,	52·5 ,,
Charcoal,	10·5 ,,
Sulphur,	7·0 ,,

"Rend-rock."

Nitro-glycerine,	40 parts.
Potassium nitrate,	40 ,,
Wood pulp,	13 ,,
Pitch,	7 ,,

"Hercules Powder."

Nitro-glycerine,	60·00 parts.
Potassium nitrate,	31·00 ,,
Potassium chlorate,	3·34 ,,
Magnesium carbonate,	10·00 ,,
Sugar,	15·66 ,,

As will be seen from these few examples, the base is in itself active, being of the class considered in the first part of this paper, *explosive mixtures.*

Like other experimenters in this domain, Nobel continued his attempts to find a suitable substitute for the inactive base Kieselgühr, and conceived the idea of adding to the nitro-glycerine the soluble variety of gun-cotton (a mixture of the lower nitrates, and *not* an explosive in the ordinary sense of the term), which he did, and produced what is now known as *blasting gelatine*. It is a translucent, elastic, yellowish-brown substance, practically impervious to water, and much more violent in its action than nitro-glycerine itself. In order to adapt it to ordinary uses he moderated the action very considerably by mixing with it potassium nitrate and wood-meal or pulp—the well-known *Geligmite*—having the composition—

Nitro-glycerine, - -	96 parts.	Blasting gelatine, 65 parts.
Nitro-cellulose, - -	4 ,,	
Sodium nitrate, - -	75 ,,	
Sodium carbonate, -	1 ,,	Base, - - 35 ,,
Wood-meal, - - -	24 ,,	
		100 ,,

Blasting gelatine and its allied explosives are now used very largely, and have, in a great measure, ousted dynamite from its former high position. They can withstand a fairly high temperature and do not freeze readily—one of the great drawbacks to the use of dynamite in cold climates—and the incorporation of the collodion with the nitro-glycerine seems to be very perfect, as no exudation takes place even under varying conditions of temperature. Water will alter them superficially only, a small portion of the nitro-glycerine being removed, but, even under the very crucial tests to which they have been subjected by experts, they have been found to show little or no sign of decomposition.

The employment of all the compounds that have come under our notice so far has been mainly confined to blasting operations, as from what has been said under gunpowder it will be seen that the action of these nitro-compounds (*vide ante*) is far too rapid and violent to admit of their application to ordnance of any description or size. Since the discovery of gun-cotton and of blasting gelatine efforts have been made to supplant gunpowder as an explosive for use with fire-arms by some suitable material, whose action would not be too rapid and which would have the virtue of being *smokeless*. To attain this end numerous substances have

been employed, but the most satisfactory are those in which gun-cotton, nitro-glycerine, and *some deterrent* material occur. As these smokeless powders are now in general use by all nations, they appear to me to be the latest stage reached in the development of the modern high explosive, and deserving of some notice. In preparing them, the gun-cotton is carefully dried and, along with the other substances entering into the composition of the powder, dissolved in the nitro-glycerine, or we might call it "gelatinised." The whole is thoroughly mixed and, after partial evaporation of the solvent, rolled into sheets repeatedly. These sheets are cut by suitable machinery into cubes or strips of various lengths according to the purpose for which they are to be ultimately employed. For small-arm powders the grains are dusted and glazed, as in the case of ordinary powder, and absolute uniformity of composition is, of course, essential, if any degree of certainty is to be attained regarding the effect of the explosion.

In the smokeless powder produced by Nobel the substances employed were nitro-glycerine and the *soluble* variety of nitro-cellulose only, no *deterrent* being used. The use of heated rollers enabled him to incorporate a very much larger percentage of nitro-cellulose with the nitro-glycerine than had hitherto been done, and the resulting powder, consisting of about equal amounts of the two ingredients, formed his well known explosive *Ballistite*. This was among the many smokeless powders submitted to the Government a few years ago when a suitable powder for use in the services was being sought for. It was not adopted, however, as the Committee of experts employed to look into the matter had in the meantime produced another powder, in which *insoluble* nitro-cellulose (*i.e.*, gun-cotton) was employed along with a solvent, instead of the soluble variety being directly mixed with the nitro-glycerine. This they adopted as the service explosive, and it is now known as *Cordite*. It composition is:—

Nitro-glycerine, - - - - -	58 parts.
Gun-cotton, - - - - - -	37 ,,
Mineral jelly (vaseline), - -	5 ,,

In making cordite the gun-cotton and nitro-glycerine are thorougly mixed together, and *acetone*, which serves as a solvent, added. Mixing is continued for some time, the required amount of vaseline added, and the whole thoroughly incorporated. The

resulting mass is rolled and squeezed through dies of various sizes according to the calibre of gun for which it is to be used, and, as it emerges from the dies, the cordite is wound on reels or drums. These "yarns" are further wound together so as to assure homogenity of structure and finally cut into lengths of the required size. The gases evolved during explosion are :—

CO_2,	25·4
CO,	37·62
N,	19·55
H,	17·43
	100

The diameter of the cords (or, for heavy ordnance, cylinders) varies from ·037-inch up to ·5-inch. In the case of cylinders they are of tubular form. As the cordite cartridge and ·303 calibre rifle are in the hands of all Her Majesty's forces it may be of interest to note that the muzzle velocity of the projectile is approximately 2,000 feet per second, the charge being 30 gms. and the bullet weighing 215 gms. The pressure exerted is 33,000 lbs. per square inch.

An unfortunate circumstance attending on the use of these powders is the corrosive action on the barrels of the guns caused by the gaseous compounds of nitrogen, which, in combination with moisture, speedily affect the interior of the bore, unless the precaution is taken of thoroughly cleansing the weapon immediately after firing.

In addition to the powders we have considered, and whose use is mostly confined to military purposes, there are several others which find employment in shot-guns and sporting rifles. Among them may be mentioned that invented by Schultze, an officer in the Prussian Artillery, and which bears his name, and also "E. C. Powder." Their composition is :—

"Schultze" Powder.

Insoluble N-C.,	32·66
Soluble ,,	27·71
Cellulose,	1·63
$Ba2NO_3$,	27·62
$NaNO_3$,	2·28
KNO_3,	2·47
Paraffin,	4·20

"E. C." Powder.

Insoluble N-C.,	53·57
Soluble ,,	1·86
Cellulose,	3·12
$Ba2NO_3$,	34·26
$NaNO_3$,	3·67
KNO_3,	1·48
Aurin,	0·55

A totally different class are the "Sprengel" explosives, which were first proposed by Dr. Hermann Sprengel in 1873. The principle of this class is "the admixture of an oxidising with a combustible agent at the time of, or just before, being required for use, the constituents of the mixture being themselves non-explosive." Though many of them are of considerable practical value and very powerful in their action, still, in the hands of the average miner they may prove exceedingly dangerous. True, the materials being kept apart, their transport offers no difficultics, but a certain degree of skill is necessary for mixing the constituents, and these obstacles have militated against their general employment. The best known among them are *Rack-a-Rock*, *Hellhoffite*, and *Panclastite*, which are composed as follows:—

"Rack-a-Rock."

Potassium chlorate,	79
Nitro-benzene,	21

"Hellhoffite."

Meta-di-nitro-benzene,	47
Nitric acid,	53

"Panclastite."

Nitrogen tetroxide,	3 volumes.
Carbon bi-sulphide,	2 ,,

The comparative strength of the various classes of explosives that I have described can best be illustrated in tabular form. It will be noticed how Nobel's *explosive gelatine* heads the list—the typical mixture—gunpowder taking last place:—

Explosive gelatine,	106·17
Hellhoffite,	106·17
Nitro-glycerine,	100·00
Gun-cotton,	83·12
Dynamite,	81·31
Rack-a-Rock,	61·71
Mercury fulminate,	50·00
Gunpowder,	28·10

I have endeavoured to show you, in the short space that is at one's disposal in a paper of this sort, the tremendous strides that have been made in the latter half of this century in the production of explosive bodies other than gunpowder. The leading part played by Nobel in this work is seen all through, and it is to his labours that we are in the main indebted for the powerful tool which is now in the hands of engineers and miners. With the employment of nitro-glycerine compounds, blasting has almost become a science, and rendered possible many gigantic undertakings which with gunpowder could not have been done. The mining industry has also received an impetus, and one has only to look at the comparative ease with which railway cuttings are now-a-days made through immense masses of hard rock to realise how much has been done to forward the progress of civilisation by the late Alfred Bernard Nobel.

In conclusion, I would acknowledge my indebtedness to the service manuals of this country and of the United States for the help they have afforded me. The particulars of Nobel's life and training I have obtained from a short biographical sketch written by one who for many years had the privilege of his personal friendship, Mr. Henry de Mosenthal.

GUNPOWDER.—Part II.

Until comparatively recent years the equation

$$2KNO_3 + 3C + S = K_2S + 3CO_2 + N_2$$

was accepted as expressing the decomposition of gunpowder as it takes place in the bore of a gun. But further investigations have shown that this by no means accounts for the number of substances which are produced, among which are potassium carbonate, sulphate, di-sulphide, sulpho-cyanate, ammonium carbonate, free sulphur and carbon, while the gaseous products include carbon dioxide and monoxide, nitrogen, sulphuretted hydrogen, and marsh gas.

The complex nature of these results led Abel and Nobel to conclude, after minute investigation, that no single equation could be held to represent the decomposition which occurs.

Indeed, they came to the conclusion that "the same description of powder, exploded several times in succession, yields products of combustion in variable proportions."

Berthelot brought forward a theory to explain these results, and considers three simultaneous decompositions as occurring. Debus, on the other hand, takes exception to all these explanations, and, from various considerations, he concludes that the combustion of gunpowder consists of *two* distinct changes, one a process of oxidation which is finished in a very short time (a fraction of a second), and the other a process of reduction requiring a comparatively long time for its completion. Taking the equation

$$16KNO_3 + 13C + 5S = 3K_2CO_3 + 5K_2SO_4 + 9CO_2 + CO + 8N_2 \quad (I.)$$

as representing the *first* stage, and remembering that a portion of the carbon and of the sulphur is left unoxidised, Debus gives as the *second* reactions which take place, requiring an appreciable time for their completion—

$$4K_2CO_3 + 7S = K_2SO_4 + 3K_2S_2 + 4CO_2 \quad (II.)$$
$$4K_2SO_4 + 7C = K_2CO_3 + 2K_2S_2 + 5CO_2 \quad (III.)$$

The metamorphosis of powder in the case of a shell bursting at once may be expressed by equation (I.), but in the bore of a gun the substances on the left hand side of equations (II.) and (III.) remain in contact, in a molten condition and at a red heat, producing, according to this theory, the results indicated above.

The possibility of two decompositions, such as are here given, resulting in the mutual reduction of the sulphate by the carbon and of the carbonate by the sulphur, with the reproduction of carbonate and sulphate of potassium, besides there being only *one* gaseous product of this reaction, namely, carbon dioxide, appeared to me to be open to discussion. To investigate the matter I proceeded as follows:—

Two varieties of gunpowder were taken, one a *fine* grain powder and the other a coarser.

Experiment 1.

2 gms. of thoroughly dry *coarse-grain* powder were taken and placed in a stout piece of combustion tubing, 40 cms. long and closed at one end. This was inserted in a small furnace, securely

fastened to the framework, and the whole surrounded by a thick cloth to prevent accidents should the tube burst. Figure 1 shows the apparatus employed.

The powder was ignited by placing the bunsen burner B under the closed end. A violent explosion occurred; the bunsen was removed, cork A immediately inserted, clip D opened, and at the same time the furnace was lighted. The *secondary* products (gaseous) of the reaction were collected in vessel C, which, at the commencement of the experiment, was filled with water, and in communication with H. The temperature of the furnace was raised to 500° C, and kept at that for 30 minutes. The resulting gases were transferred to gas burette, and on analyses gave the following:—

50cc.	H_2S	= 2·0 parts by volume.
taken for	CO_2	= 7·6
each analysis	O	= 0·0
	CO	= 8·4
	N	=82·0
		100

The solid residue left in the tube was found to contain K_2SO_4, but no K_2CO_3 could be detected. Some sulphur and carbon remained unacted upon, and a *very faint* odour of sulphuretted hydrogen was noticed on opening the tube. A copious evolution of H_2S, on addition of HCl, pointed to the presence of K_2S.

The second experiments were performed with the *fine grain* powder in exactly the same way, and (as also in previous case) the tube, after the initial explosion, was seen to be coated with a fine white powder interspersed with black particles of unburnt carbon. (In both cases the tube cracked on cooling at the point where the ignition of the powder had taken place). Analyses of the gases gave—

H_2S	= 0·4 parts by volume.
CO_2	= 6·8
O	= 0·0
CO	= 9·2
N	=83·2
	100

The solid residue was identical with that given by the coarse, but the amount of material was, in neither case, sufficient to allow of a quantitative determination being made.

Second Series of Experiments.

The *solid* products C, S, K_2SO_4 and K_2CO_3, as represented in equations (II.) and (III.), were mixed together and heated in an atmosphere of nitrogen to a temperature of 500° C., the gaseous products being collected as before. Analyses gave as result—

H_2S	= 0·4 parts by volume.
CO_2	= 0·4
O	= 0·0
CO	= 10·0
N	= 89·2
	100

Figure 2 represents the apparatus used.

A—Flask with NH_4CE and KNO_2 generating N.*

B—Tube with pumice stone saturated with H_2SO_4.

C—Drying tower.

D—Furnace with tube and contents.

A brisk current of nitrogen was passed through the tube till perfectly free from all traces of air. Pinch-cock at G was then closed, E and F connected with tube at H, and the tube and its contents heated.

In the residue was found free carbon, and on dissolving in water traces of H_2S were got. On treatment with HCl, a copious evolution of CO_2 and of H_2S, showing presence of K_2S in quantity, and only a small amount of K_2S_2, as no S was deposited even on warming the solution. K_2SO_4 was present, but no K_2CO_3 could be detected. This experiment was repeated with amounts of material in accordance with equations (II.) and (III.).

(*a*) 5 gms. of a perfectly dry mixture of

0.50 gms.,	C
3·30 ,,	K_2CO_3
4·19 ,,	K_2SO_4
1·30 ,,	S

were taken and heated in apparatus as in fig. 2 in an atmosphere of nitrogen. The mixture fused and remained in that condition

* Note.—This mixture evolved a considerable quantity of NH_3 on mixing, which became less as the action proceeded. The H_2SO_4 was necessary to absorb this.

throughout the experiment Much sulphur passed over unchanged. Temperature, 500° C. Time of heating, 45 minutes. The gases evolved were composed of—

H_2S = 17·2 parts by volume.
CO_2 = 49·6
O = 0·0
CO = 7·2
N = 26·0

100

(*b*) The amount of CO_2 evolved seemed to point to the air not having been thoroughly expelled from the tube prior to the heat being applied, so two other experiments were made with 2 gms. of the mixture, the time of heating being 30 minutes.

The result of these gave as the composition of the gaseous products—

H_2S = 4·0 parts by volume.
CO_2 = 30·0
O = 0·0
CO = 3·9
N = 62·1

100

The residue in the tube was identical in all these experiments. It was extremely deliquescent, contained much unburned carbon, but practically no sulphur. On dissolving in water H_2S was evolved in small quantity, the resulting solutions being yellow in colour. In it were found K_2S, K_2S_2,* K_2SO_4, but no K_2CO_3 could be detected.

Summarising these results we get—

Secondary Products of Gunpowder.

	Coarse Grain.	Fine Grain.
H_2S,	2·0	0·8
CO_2,	7·6	6·8
O,	0·0	0·0
CO,	8·4	9·2
N,	82·0	83·2
	100	100

* K_2S_5 is very probably also present as solution, gives a *red* ppt. with Pb2NO$_3$ changing to black. This, according to Berzelius, is only got from a lead salt and the penta-sulphide.

Products from heating C, S, K_2CO_3, *and* K_2SO_4.

	I.	II.	III.
H_2S,	0·4	17·2	4·0
CO_2,	0·4	49·6	30·0
O,	0·0	0·0	0·0
CO,	10·0	7·2	3·9
N,	89·2	36·0	62·1
	100	100	100

The conclusions arrived at from these experiments may be briefly stated.

The decompositions occurring with the same powders, and under the same conditions, clearly vary considerably, though it will be noticed that the *total* amount of CO and CO_2 in each case is identical, H_2S being the variable.

Looking at the second series of results we find even greater discrepancies, but all through the production of CO is apparent, thus making equations (II.) and (III.) incomplete, as was expected. In (I.) the quantities taken were roughly estimated, so this, as regards the production of CO, may be neglected. H_2S appears constantly, and in very appreciable amounts. The difference of nearly 20 per cent. of CO_2 in (II.) from that in (III.) is accounted for by the incomplete removal of air as before noticed. Regarding the solid residues, there appears to be *complete* reduction of the K_2CO_3, none being found in any of the aqueous extracts. The gunpowder residue gave no indication of the presence of K_2S_2, nor did the first of the second series, K_2S *only* occurring in these cases, while in (II.) and (III.) the presence of the higher sulphides of potassium was very apparent. Whether these consist of K_2S_2 only, or of other poly-sulphides as well, is yet to be seen, though from what has been said, and particularly from the production of the red sulphides of lead referred to in the footnote on page 22, it looks as if the di-sulphide was not alone. One would have expected a closer agreement in composition of the gases evolved in (II.) and (III.), but, despite the fact that the mixtures taken were identical and the conditioning circumstances the same, it would appear to be impossible to properly represent the decomposition of such a mixture by an equation.

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Note on an Analysis of Human Gastric Juice.

By W. R. Lang, B.Sc., F.C.S., Chemical Laboratory, University of Glasgow. (*Communicated by* Prof. M'Kendrick.)

(Read March 15, 1897.)

In the autumn of 1895 I received from Professor M'Ewen several samples of gastric juice marked "Chalmers' Gastrostomy." The samples were obtained under most favourable circumstances, being drawn off through an aperture made in the abdomen and stomach of the patient; the juice was almost pure, and nearly free from suspended matter. My analysis was mainly directed towards ascertaining whether or not free hydrochloric acid was a constituent of the fluid, and the following were the reactions I employed :—

(1) With methyl violet the sample gave a distinct blue coloration, showing the presence of a mineral acid. Supposing the acidity to be due to lactic acid, this reaction would not take place, as on trying a dilute solution of lactic acid with this reagent no blue colour was produced.

(2) On treating an alcoholic solution of phloroglucin and vanillin (1 grm. of the former and $\frac{1}{2}$ grm. of the latter made up with 50 c.c.'s rectified spirits) with the gastric juice and evaporating slowly on a water-bath, a red colour was produced. Dilute hydrochloric acid gave the same result; lactic acid none.

In the opinion of some authorities the presence of free hydrochloric acid is attributed to the decomposition on evaporation of the chlorides present in the gastric juice by free lactic acid. With a view to ascertain whether this could happen or not, I evaporated solutions of chloride of calcium and lactic acid with both of the above reagents with a negative result. I also tried solutions of chlorides of the alkalies of various strengths with lactic acid under similar conditions, but in no case could I detect the slightest trace of free hydrochloric acid. These experiments clearly showed, therefore, that no such decomposition of the chlorides as was suggested could account for the reactions given with the gastric juice and the above reagents; and, consequently, the presence of free hydrochloric acid in the samples examined is clearly proved.

8

SOME ESTERS OF ARSENIOUS ACID. PART II RESORCINYL ARSENITE.

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BY

WILLIAM ROBERT LANG

AND

JOHN OBINS WOODHOUSE.

From the Proceedings of the Chemical Society, 1909. Vol. 25

180. "Some esters of arsenious acid. Part II. Resorcinyl arsenite." By William Robert Lang and John Obins Woodhouse.

Continuing the experiments described in a previous communication (Lang, MacKey, and Gortner, *Trans.*, 1908, **93**, 1364), but using one of the dihydric phenols, quantities by weight of resorcinol and of arsenious oxide corresponding with the equation below were heated to the melting point of the former in a distilling flask, connected through a weighed flask with an exhaust pump. The temperature was kept constant, and the arsenic slowly dissolved in the melted resorcinol, yielding an amber-coloured fluid becoming darker as the heating progressed, the pressure being 60 mm. The water evolved in the reaction, $3C_6H_4(OH)_2 + As_2O_3 = (C_6H_4O_2)_3As_2 + 3H_2O$, collected in the trap and was weighed as a check, due precautions being taken to prevent loss. After heating for fifty-five minutes the mixture was allowed to cool, broken up, and extracted

with hot toluene, which removed from it some resorcinol. The residue was dissolved in dry ethyl alcohol, in which these esters are soluble, when an immediate precipitate of arsenious oxide was produced. Analysis of the substance obtained on evaporation in a vacuum of the alcoholic extract proved it to contain from 5 to 6 per cent. of arsenious oxide in excess of that required by the formula $(C_6H_4O_2)_3As_2$, showing that arsenious oxide dissolved in the ester formed. To prevent this, an excess of resorcinol was employed, namely, 100 grams, and 50 grams of arsenious oxide heated with it as before, the proportions of the former to the latter being, according to the equation supposed to represent the reaction, 100 to 60; in this way an amount of resorcinol corresponding with 10 grams of arsenious oxide would, of necessity, remain unacted on and be readily extracted from the ester by a specific solvent. After an hour's heating, the solidified mass was broken up and digested in a reflux condenser with dry toluene, which extracted a considerable proportion of resorcinol. This treatment was repeated until no more resorcinol could be obtained on evaporation of the solvent. The resorcinol-free mass was analysed as follows. About 1 gram was treated with water, which caused its immediate decomposition, the solution acidified with hydrochloric acid, and the arsenic precipitated as sulphide, dried on a tared filter, and weighed. The results of numerous analyses, which closely corresponded, gave:

Found, As = 31·9. $C_{18}H_{12}O_6As_2$ requires As = 31·65 per cent.

Resorcinyl arsenite closely resembles hardened gelatin in appearance, melts at 24°, and has a specific gravity of 1·9. It is soluble in methyl, ethyl, propyl, and butyl alcohols, but insoluble in ether, chloroform, benzene, or toluene. Water, however, immediately decomposes it.

The same experiments were tried with quinol, but, so far, without success.

R. CLAY AND SONS, LTD., BREAD STREET HILL, E.C. AND BUNGAY, SUFFOLK.

A CENTURY OF CHEMICAL PROGRESS

INAUGURAL ADDRESS

DELIVERED JANUARY 26th, 1901

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Reprinted from the "University of Toronto Monthly,"

Vol. I., No. 6

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1901

A Century of Chemical Progress.

BY PROFESSOR W. R. LANG.

THERE are few branches of science which have progressed so rapidly in the last hundred years as the one I have the honour to profess in this University. Looking back over this period one sees in existence a very different state of affairs, socially, commercially and otherwise, than is now with us, and it is no exaggeration to say, that much of the present comfort enjoyed by all classes, is due to the advance of physical and chemical science. Biology even, electricity certainly were in their infancy in 1800. Chemistry, as we know it now, almost equally so. The old alchemistical idea of "phlogiston" had received a decent burial, though its memory was kept green by Priestley till his death in 1804, and the medical chemists, whose search for the "elixer vitæ" had occupied their attention since the middle ages had given up the quest for more profitable inquiry. The search for the "philosopher's stone," which was to convert all baser metals into gold, had been the main object of the experiments of a certain class of chemists, but such men as Black, Cavendish, Scheele, Priestley and Lavoisier—who fell a victim to politics during the French Revolution—were studying the composition of matter for the sake of knowledge itself. That science was on the verge of entering on a new era is evidenced by the fact that in 1800 the Royal Society (founded 1663) commenced its "Catalogue of Scientific Papers." Chemical knowledge at that period was limited to a few isolated facts. Oxygen and hydrogen had been prepared, and the composition of air and water and of a few minerals was known, and a right understanding of the general characters of acids, bases and salts had been only recently arrived at.

At the present day, when the electric current is now used so extensively in many chemical operations and manufactures, it is of interest to note that the first experiments towards the decomposition of water into its constituent elements, oxygen and hydrogen, by this means were made in 1800 by Nicholson and Carlisle. Following on this Humphrey Davy, who in 1801 was appointed Professor of Chemistry at the now famous Royal Institution of London, applied the current from his galvanic battery to the decomposition of damp caustic potash and soda. In this way he obtained at the negative pole metallic globules, which by subsequent experiments he found could be reconverted into the alkali from which they had originally been prepared. By similar means he isolated the elements barium, strontium and calcium from the common "earths," and found that these in combination with the gas chlorine—discovered by Scheele—gave soluble saline bodies, of which common salt may be taken as the type.

Davy was at that time instrumental in proving that oxygen, which had been considered the acid-forming element, was not necessarily a constituent of all acids. Chlorine was supposed to be an oxide of hydrochloric acid, but all experiments which he performed to find oxygen in chlorine proved decisively that it was an elementary body. About this time also Curtois, a Parisian soap-boiler, when preparing soap with alkali obtained from sea-weed found indications of a substance hitherto unnoticed. This he sent to Davy, who discovered its elementary character and its resemblance to chlorine, and thus iodine came to be added to the rapidly growing list of simple substances. In 1826 Balard added one more to the number by his discovery of bromine in the mother liquor or "bittern" left after the removal of sea-salt from sea-water by evaporation.

Contemporaneously with Davy's earlier researches, John Dalton, a Manchester schoolmaster, enunciated his famous theory, which has remained the fundamental hypothesis of chemistry to this day. According to this doctrine, matter is composed of minute particles or "atoms," each with a definite relative weight, and compounds are formed by these atoms of different elements becoming closely united to form a homogeneous whole. Other chemists had noticed that the same compounds always contained the same elements in the same proportions by weight, and that when more than one compound could be got containing the same elements, but in different proportions, the proportion in which the one element combined with the other in the second case was a multiple by a whole number of the proportion in which it combined in the first case. All this Dalton's hypothesis accounted for. Thomas Thomson, the professor of chemistry in the University of Glasgow, was the first to teach Dalton's views, and he incorporated these ideas into his "System of Chemistry," published in 1805. In his "Chemical Philosophy," published a few years afterwards, Dalton expresses his ideas thus: "Chemical analysis and synthesis go no farther than to the separation of particles one from another, and to their reunion. No new creation or destruction of matter is within the reach of chemical agency. We might as well attempt to introduce a new planet into the solar system, or to annihilate one already in existence as to create or destroy a particle of hydrogen. All the changes we can produce consist in separating particles that are in a state of cohesion or combination, and joining those that were previously at a distance." Thomson, Berzelius, Prout, Stas and Dumas all proceeded to determine what these constant weights were in which the elements combined together, and a series of numbers was obtained and termed atomic weights, or more properly, equivalent weights.

Hitherto little notice had been taken of the volume relation in which elements combined. Gay-Lussac and Avogadro noticed the definite proportions in which gases combined together, which later became extended to elements in the gaseous state that were at ordinary temperature liquids or solids. To enter into further particulars, however, regarding the facts relating to atomic weights, made evident by careful study of those volume relations, would be beyond the scope of this

lecture. Equally so would be any detailed explanation of the facts established by the researches of Dulong and Petit regarding the relation between the atomic weights of the elements and their capacity for heat. Suffice it to say that this relation has proved instrumental in ascertaining those relative numbers, a true knowledge of which is indispensable alike to the physicist and the chemist. The theory enunciated by Avogadro, previously referred to, that equal volumes of gases contained an equal number of particles or molecules, received confirmation from the researches of Thomas Graham, of University College, London, into the subject of gaseous diffusion. Experiment showed that the rate of the diffusion of different gases through some porous material varied inversely as the square roots of their respective densities. Graham also contributed greatly to our knowledge of liquid diffusion, and his researches and views on the constitution of the phosphoric acids are now classic.

At the beginning of the century Germany had produced few chemists; at any rate none of the first rank. Liebig may, perhaps, be considered its first great man, and he in his youth received his instruction in the laboratory of a French chemist, Gay-Lussac. In 1837, when her late Majesty Queen Victoria of sacred memory ascended the throne, he was in the height of his fame. To him we owe much of the impetus which was given to the study of scientific chemistry in England, and to him the physiologist, the manufacturer and the agriculturist are indebted for a great portion of their present knowledge of the practical application of it to their varied needs. He it was who devised the method still in use for the determination of the composition of "organic" compounds. Wöhler showed at this time by his synthesis of urea—a substance hitherto considered as purely the result of vital action—that "organic" chemistry must be regarded as the chemistry of compound radicles. Liebig and Dumas were at one with Wöhler in this, and formally announced their adhesion to his doctrines at a séance of the Académie des Sciènces de Paris in 1837. The enormous strides made in the development of this branch of chemistry cannot but strike the most callous observer as one of the marvels of the century. From the synthesis of urea in 1828 by Wöhler, and of acetic acid by Kolbe in 1845 down to the present day, when dyes of every shade and tint, explosives of all kinds, drugs, sugar, and even indigo can be built up in the laboratory by artificial processes, the development of this department has been phenomenal. And how has this come about? The conception of radicles led to an incalculable amount of research into the constitution of organic compounds, and the ways in which radicles were linked together and to elementary atoms. Compounds were broken down and again reconstructed, and the methods of causing these combinations to take place gradually became perfected. It may safely be said that the manufacturers of to-day owe much, if not all, of their success to the investigation following on these theoretical conceptions of the distinguished chemists I have named.

The old system of formulæ, based on Dalton's atomic hypothesis, came

in for reconstruction about the middle of the century. Gerhardt (1843) was the first to seriously discuss the question, closely followed by Williamson (1850). It was some time, however, before the system deduced from their views was generally accepted. Hofmann was the first to adopt it in his lectures, and in 1864 Dr. Odling, the President of the Chemical Section of the British Association, congratulated the section on the agreement that had been arrived at amongst chemists as to the combining proportion of the elements and the molecular weights of their compounds. Observation of the natural families into which the elements grouped themselves led to the enunciation of what is now known as the "Periodic Arrangement of the Elements." In 1864, Newlands, of London, showed that when the elements were arranged in the order of the numerical value of their atomic weights, their properties, physical and chemical, varied in a recurrent or periodic manner. Thus it was seen that the element eighth in succession from another usually resembles it closely. Newlands termed this arrangement the "Law of Octaves." In 1869, Mendeléeff, of St. Petersburg, contributed further facts concerning this periodic arrangement of the elements and their study at this day is based on that now fully recognized system of classification. Both Newlands and Mendeléeff predicted the existence and physical and chemical properties of many undiscovered elements which would go to fill the blanks in the table. When gallium, scandium and germanium were isolated they were found to correspond to the elements predicted by Mendeléeff, and to which he had assigned the names, "eka-boron," "eka-aluminim" and "eka-silicon."

The phenomena exhibited by many substances in their action on polarized light has led to ideas regarding the arrangement of atoms in space. To Pasteur, and more notably Le Bel and van't Hoff, is due the credit of bringing before chemists a hypothesis which has had an enormous influence in the progress of organic chemistry.

The study of substances in solution has provided a means of determining molecular weights. Pfeffer, the botanist, in 1878, performed an important series of experiments with membranes deposited by chemical means in the pores of unglazed earthenware, and found that if weak solutions of salts were placed outside such a vessel water would diffuse through while the dissolved substance would not. This was due to the "semi-permeability" of the membrane employed. Van't Hoff, in 1887, in studying the theory of dilute solutions, found that the semi-permeable membranes served to measure the pressure due to the dissolved substance. From an accurate study of substances in dilute solution and of their behaviour with regard to their passage through extremely thin porous membranes it is now evident that there exists the closest possible analogy between the state of substances in solution and the same in the gaseous condition. As the result of experiments on the conductivity of substances in solution for electricity, Arrhenius (1888) has shown that when an electrolyte, such as common salt, is dissolved in water it dissociates partly into the separate *ions*, a name devised by Faraday, and signifying the "things that go," namely sodium and chlorine. These

views have been strongly upheld by Ostwald and others, and are supported by the facts rendered apparent by the behaviour of substances in solution as regards diffusion, the lowering of the vapour-pressure and the depression of the freezing point of the solvent.

Davy, it has been pointed out, obtained the alkali metals by electrolytic decomposition of their compounds. Electrolytic methods of analysis and the application of electricity to commercial processes and to more purely scientific research have gradually become of more and more importance and interest. If electricity is passed through a conductor, such as a metal bar, the current passes along or through the metal which itself does not move or suffer any apparent alteration. But when a current is passed through an electrolyte it is transported by the moving *ions*. The theory before referred to, that a portion of the substance in solution is in a dissociated state, goes far to explain the phenomena attendant on electrolyses. Though it seems difficult to imagine that in the case of a solution of sodium chloride there can exist sodium and chlorine in the free state, especially as the metal sodium has such a violent chemical action on water, yet, according to the electrolytic dissociation theory, we must consider that the different constituents of the sodium chloride do exist as separate atoms but having enormously high charges of electricity. When, keeping to sodium chloride as our example, a current is passed, the sodium atoms charged with positive electricity travel to the negative pole and there give up their charges, appearing then as molecules of sodium possessing the properties usually associated with that element. Similarly the chlorine *ions* charged with negative electricity travel to the anode, or positive pole, give up their charges and appear as ordinary chlorine.

While these principles were gradually being unfolded and the newer ideas concerning matter were becoming more familiar, fresh discoveries of new elements were being made, It must be remembered that the compounds of many elements were known while as yet the elements themselves had not been isolated. Alumina and silica were known long before the elements aluminium and silicon were isolated ; so also with fluorine, one of the chlorine group. Fluorine was known to exist widely diffused in nature in many minerals and in small quantities in plants and animals, but on account of its great chemical activity it had not been isolated, as had been its neighbours, chlorine, bromine and iodine. Davy and Scheele had both recognized its resemblance to these elements, but it was not till 1886 that Henri Moissan, professor of chemistry at l'École de Pharmacie in Paris, succeeded in electrolyzing a mixture of hydrofluoric acid and hydrogen potassium fluoride in a platinum vessel. In 1897, when the British Association met in this city, Professor Méslans, for many years assistant to Moissan, gave a demonstration of the properties of fluorine here in this lecture-room.

The last decade has been fruitful in the discovery of other elements hitherto unsuspected, notably the new atmospheric gases, argon, neon, krypton and xenon. In 1775, Cavendish in his "Experiments on Air," published in the *Philosophical Transactions*, pointed out that in the air

there was a small quantity of a gas, "not more than 1/120 of the whole" of what we now call the nitrogen of the atmosphere, which could not be made to combine with oxygen. The question as to what this was lay unanswered for more than a century, when, in 1894, Lord Rayleigh and Professor Ramsay solved the problem by isolating argon from atmospheric nitrogen. They were led to this discovery by noticing that atmospheric nitrogen was denser than nitrogen prepared from chemical sources, such as ammonium nitrite. By passing a stream of atmospheric nitrogen over heated magnesium the nitrogen was absorbed and a residue remained, which could not be induced to enter into combination with anything. The amount of this new element in the air, whose discovery caused so much excitement in the scientific world, was found to correspond very nearly to the small portion of gaseous matter that remained uncombined after sparking atmospheric nitrogen with oxygen, and which Cavendish had spoken of more than one hundred years previously. This discovery of argon led to a further research into certain minerals, which, when treated with dilute acid, evolved a gas which was supposed to be nitrogen. It proved, however, to be another new element, previously indicated as being present in the sun's atmosphere by Lockyer, and named by him helium. These discoveries did not, however, end here, as Ramsay and Travers, in experimenting with liquid air as a convenient source of argon, discovered three new gases, which they named krypton (hidden), neon (new), and metargon.

Turning now to the interesting subject of the liquefaction of gases, we find that since the beginning of this century numerous experimenters have been trying to reduce the more commonly met with gaseous substances to the liquid condition. The so-called permanent gases, which, up to a decade or so ago, resisted all attempts at liquefaction, have now succumbed to the advance of experimental science. In 1805 Northmore is stated to have liquefied chlorine by compressing it in a brass condensing syringe with a glass receiver. Then in 1822 Cagniard-de-la-Tour observed that certain liquids, such as alcohol and water, when heated and kept under pressure, became apparently reduced to a vapour, occupying from two to four times the original volume of the liquid. This led to the classical researches of Andrews, of Belfast, on "The Continuity of the Gaseous and Liquid States of Matter," set forth in the Bakerian Lecture (Phil. Trans., 1869, Part II). In the following year Faraday succeeded in liquefying chlorine, sulphur dioxide, hydrogen sulphide, carbonic acid, ammonia and many other substances previously known only in the gaseous condition. There only remained hydrogen, oxygen, nitrogen, carbon monoxide, marsh gas and nitric oxide; these were called the "permanent gases." In connection with the liquefaction of carbonic acid the name of Thilorier stands out prominently. By means of pressure alone he obtained this in the liquid form, and by causing it to evaporate rapidly through a narrow orifice obtained it in the solid state. This was the first instance of a substance, gaseous at the ordinary temperature, being seen as a solid. Faraday, in 1845, continued his attempts to liquefy the remaining gases, and in his experi-

ments came very near to anticipating Andrews in his famous researches and the principles deduced therefrom. Briefly stated, Andrews found that there was a certain temperature peculiar to each gas, above which no amount of pressure could cause liquefaction. This he termed "the critical temperature." From this it will be seen why so much difficulty was experienced in attempting the liquefaction of the six permanent gases, as, up to that time, the lowest temperature obtainable had been above the critical points of all of them. Towards the close of 1877 Cailletet, of Chatillon-sur-Seine, and Pictet, of Geneva, communicated simultaneously to the Académie des Sciènces de Paris that they had succeeded in liquefying oxygen, carbon monoxide and nitric oxide Cailletet subjected the gases to considerable pressure, thereby reducing greatly their volume; on suddenly relieving the pressure expansion and consequent cooling took place, and a portion of the gas appeared in the form of minute drops. Nitrogen and hydrogen now alone remained; the former yielded in 1883 to Professors Wroblewski and Olszewski, and hydrogen succumbed in 1895 to Professor Dewar, of the Royal Institution in London. The principle involved in liquefying these gases is as follows: we have seen how liquid carbonic acid, if allowed to expand, is cooled down sufficiently to enable it to become actually solid. Supposing, then, that air or hydrogen is compressed under 180 atmospheres or so (2,500 lbs. to the square inch), and the pressure gradually released, the temperature of the issuing gas will be lowered considerably. By allowing this cooled gas as it issues to pass over a large surface of copper coils conveying the compressed gas from the cylinder containing it to the expansion valve the gas becomes still more cooled down, a cumulative effect is produced, and finally the issuing gas arrives at the point of exit at so low a temperature that it becomes liquid. Different forms of apparatus have been devised by Hampson of London, Linde of Munich, and by Dewar, and are now used for producing liquid air in fairly large quantities, but the principle involved in each is the same. By the rapid evaporation of liquid hydrogen Dewar succeeded in obtaining it as a snow-white solid.

Thus far I have only discussed the development of what might be called scientific chemistry. The field of industrial chemistry is so wide that only a short reference can be made to the advances that have been made during the past hundred years. It must be pointed out, however, that the growth of chemical industry owes much of its progress to the reasonings and researches of the theoretical chemist.

Among the branches of industry which have advanced greatly might be mentioned the soda industry, with which the production of chlorine, and consequently bleaching-powder, is closely associated. The Leblanc process, invented during the Napoleonic wars, at the end of the eighteenth century, for the production of alkali—essential in soap-making and other industries—from common salt has found a strong rival in the ammonia-soda process, first introduced by Solvay in Belgium, and brought to a high state of perfection by Brunner and Mond in England. An electrolytic process is also employed, common salt being converted directly

into caustic soda and chlorine. Electricity is also made use of for the production of aluminium, which metal is now extracted in large quantities from alumina, both on the continent of Europe and in Scotland. Its uses are many, and the peculiarly light metal which twenty years ago was looked upon as a curiosity, is now as familiar to us as copper or iron. The electric current is also employed for making calcium carbide from lime and coke. Though known since 1839, this substance had only been produced in the laboratory, and it is merely within the last ten years that it has become of commercial importance as the source of acetylene gas for illuminating purposes. To electricity we are also indebted for the production of chemically pure copper for electro-plating and gilding, and for the production of the highest of all temperatures, that of the electric arc. This temperature has been made use of in the electric furnace, more particularly by its inventor, Henri Moissan, for studying the effect of high temperatures on various substances, and with its aid he succeeded in manufacturing diamonds. Unfortunately, or perhaps fortunately, for if diamonds could be readily and cheaply made, then their value as ornaments would vanish—they can only be obtained very small, but diamonds they are despite their minuteness. The electric furnace is also used in many other departments of chemical industry.

The mineral oil industry, too, is one of great importance. Huge quantities of crude petroleum are found in the earth's crust. The first discovery of it was made by Playfair of Edinburgh in Derbyshire, but that source was soon exhausted. The source of supply is now from this continent and from eastern Europe. The production of oils from the distillation of shales is carried on in Scotland at Broxburn and elsewhere. Shale is a carbonaceous mineral which appears to have been formed from the remains of marine animals mixed with argillaceous mud and consolidated into a slaty mass. The Scottish shales, typical of their class, are below the coal measure along with strata of marl, limestone and sandstone.

To the advance in chemistry the agriculturalist is indebted for the increased crops he is enabled to take off his land. Liebig was the first to introduce the employment of artificial or chemical manures. Nitrate of soda, potash salts, and sulphate of ammonia obtained from gas-works are all employed as fertilizers, and the effect of these manures on crops has been carefully studied on experimental farms by Gilbert and Lawes.

Metallurgical processes, too, have made great progress. The extraction of gold from its ores is no longer carried out solely by the rough and ready mechanical methods by which our forefathers washed the sand of gold-bearing streams or subjected crushed auriferous quartz to the process of amalgamation. Plant for chemically separating gold by means of chlorine or of potassium cyanide is now found all over the world and the so-called "tailings" left from amalgamation processes in large quantities in the vicinity of gold-workings have proved a fruitful source of the precious metal when subjected to present day chemical treatment. The iron and steel industries have kept pace with modern chemical progress, the Bessemer process and the Siemen's-Martin process may be

mentioned as examples of improvements in methods. Not only have producers perfected to the best of their ability the processes employed for making iron and steel, but the furnace gases—formerly allowed to escape into the air—are now treated in such a way as to extract from them many useful substances which are of themselves of great market value.

As that of the chief actor in the development of the modern high explosive the name of Alfred Nobel must be a familiar word in all civilized countries. Ordinary black gunpowder is now seldom used except for producing the slow rending action required in blasting the faces of quarries, where a shattering effect would be undesirable. Schoenbein discovered gun-cotton in 1865 and nitro-glycerine was first made by Sobrero in 1847. Nobel made these nitro-compounds his special study, and in 1866, by absorbing nitro-glycerine in a porous siliceous earth known as kieselguhr, produced a brown pasty substance, and named it "dynamite." The chief constituents of the modern explosives, blasting-gelatine, cordite, gelignite and ballistite are gun-cotton and nitro-glycerine. The discovery of blasting-gelatine was accidental and deserves recording. Nobel, when in his laboratory experimenting with nitro-glycerine, cut his finger slightly, and to cover the wound applied collodion, which is a solution of nitro-cellulose in ether, to the part affected. Having done so he emptied the contents of the phial into the vessel which held the nitro-glycerine he was experimenting with. The mixture became gelatinous, and thus accidentally came about the discovery of one of the most used ingredients of modern explosives. Lately we have heard much about lyddite and its effects. This is also a product of the last decade in so far as its use as an explosive is concerned, though it has been employed for dying silk for many years.

I have endeavoured to show in this short address to what an extent scientific and industrial chemistry has progressed during the century now gone. It would be interesting to speculate as to future developments. The atomic theory which has so long been our chemical creed may be overthrown as was the theory of philogiston. Elements may no longer be regarded as simple substances and may even be looked upon as different forms of one ultimate kind of matter, or again as varying modes of motion. Speculation and theories regarding this have even now been advanced by men eminent in the world of science. Chemistry and physics are drawing closer together and the investigation of physico-chemical phenomena is occupying the attention of many workers. Great have been the advances made in pure chemistry, and to no less a degree has the application of these principles to industrial chemistry progressed. I feel I cannot close without some reference to the part that may be taken by chemists in the development of the natural resources of Canada, and more particularly of this province. I see from that useful volume a "Handbook of Canada" published by the local executive of the British Association meeting of 1897 that our province is possessed of almost untold mineral wealth. The metals gold, silver, copper, nickel, lead and iron are in abundance. Of sulphur in combination there is plenty, while

coal, mineral oil, phosphates and common salt also are found. The search after the precious metals, mining, the production of copper, iron and nickel are all departments of industry in which many graduates of the University have found and will, I venture to think, continue to find employment. It is to the men we send forth from this institution that we must look for the proper exploitation of our natural resources. While in past years most of our graduates entered the professions of medicine, law or of teaching now a large proportion are going, not only into mining and the other branches of engineering, but also into manufactures and commerce. The future of this country is in the hands of these men. Now that the School of Science has become an integral part of the University and constitutes our faculty of applied science, a stronger tie has been created between this department and that presided over by my colleague Professor Ellis than was possible heretofore. It should be the aim of the departments, then, to give our students a thorough all-round training in the principles of chemistry, not omitting reference to the practical application of these principles to the arts and manufactures. A chemist thoroughly trained in his subject by a course of study such as can be obtained in any of our universities is the man who is most fitted to apply his knowledge to whatever branch of industry he may find himself engaged in after he leaves his *Alma Mater*. I have heard it advocated that the universities and technical colleges should employ special lecturers, expert in their several spheres of chemical industry, to instruct students in the particular branch which it is to their ultimate intention to take up as their life-business. Where, I ask, are such men to be found? Is it likely that a manufacturer will enter into all the details of improvements in his own business that he has, after much experience, introduced for the benefit of his own or his employer's profit? In these days of keen competition, and of earnest striving to gain even a modest competency, any particular detail or device which will ensure a better yield of material or the production of a superior article than one's rivals in trade can produce is zealously guarded, as well it might be.

A general knowledge of the principles of the subject is the first great essential and whether it be metallurgy, brewing, calico-printing or dyeing that the young graduate proceeds to, he will always be able to adapt himself to his new surroundings and be of more use in improving the processes in which he is interested than if his whole time had been spent learning the details of his special work to the exclusion of the great general principles involved in the science. The man with energy and application, but whose academic and scientific training has been nil, has hitherto in many cases succeeded in coming to the front in whatever industry or business he may have taken up, how much more, then, may we expect to see the scientifically trained graduate (*ceteris paribus*) become a successful worker in any of the many great fields open to him.

10

THE INTERACTION OF HYDROGEN SULPHIDE AND SULPHUR DIOXIDE.

BY

WILLIAM ROBERT LANG

AND

CHARLES MACDONALD CARSON.

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From the Proceedings of the Chemical Society, 1905. Vol. 21.

86. **"The interaction of hydrogen sulphide and sulphur dioxide." By William Robert Lang and Charles Macdonald Carson.**

When hydrogen sulphide is passed into an aqueous solution of sulphur dioxide for several periods of from two to three hours on successive days, a milky solution is obtained which is termed Wackenroder's solution (Wackenroder, "On Pentathionic Acid," *Arch. Pharm.*, 1846, 48, 272, 140; Berzelius, *Jahresbericht*, 1847 27, 36). This has been investigated by Debus (*Trans.*, 1888, 53, 278), who proved the pre-

sence therein of sulphur, and sulphuric, trithionic, tetrathionic, and pentathionic acids, and probably hexathionic acid. The salts of these acids were examined by Hertlein (*Zeit. physikal. Chem.*, 1896, 19, 287), who described methods for their separation and their physical properties. The explanation given by Debus for the formation of the polythionic acids is that tetrathionic acid is a direct product of the reaction of hydrogen sulphide on sulphurous acid, and that the other acids are formed from it by various subsequent reactions.

In order to investigate this, the reaction was effected, not in solution, but in the presence of a very little moisture, without which the gases do not interact. A large flask was surrounded with snow, a little moisture blown in, and the two gases then passed in at about equal rates for from two to three hours. A heavy yellow deposit, formed in the body of the flask, but not in the neck, was probably due to condensation of water having taken place only on the colder portions of the glass. This yellow material resembled ordinary sulphur, was dry to the touch, and quite brittle. On treatment with cold water, a milky liquid was obtained and the substance became stringy; this product, when boiled with water, was rendered soft and elastic.

Deposits formed by the above methods at different times, on being heated to 100° for an hour, lost from 25—30 per cent. by weight, and on estimating the sulphur compounds contained in them (as sulphuric acid) the amount never exceeded 1 per cent. Weighed quantities of the yellow material were allowed to remain in both open and closed tubes for several days at temperatures below 0°, but no change was noticeable in any case. When heated at 100°, the same loss of weight was observed as before; the presence of hydrogen sulphide could in no case be detected. Since the residue, after heating, contained more than 99 per cent. of free sulphur, it may be concluded that the polythionic acids were present in extremely small amounts.

Several quantities of the yellow material were next placed in stoppered bottles at the temperature of the room. After one day, the sulphur had become pliable and elastic and was covered with an oily liquid having an acid reaction, while a strong odour of sulphur dioxide was perceptible on removing the stoppers. The amount of this liquid seemed to increase after the second day, and this was proved to be the case on estimating the sulphuric acid present in quantities which had stood for one and two days respectively, and which had afterwards been heated at 100°. This liquid was then obtained in larger quantities, and was found to have a sp. gr. usually above 1·35, and to correspond with what is commonly called pentathionic acid, and which Debus showed to be a mixture of polythionic acids. Around the neck of the bottles, while below 0°, colourless crystals had formed: these were in such small amounts that their composition was not determined,

although, on warming, they gave off sulphur dioxide and left a deposit of sulphur.

It would appear from the above experiments that the action of gaseous hydrogen sulphide on gaseous sulphur dioxide produces first sulphur and water according to the equation,

$$2H_2S + SO_2 = S_3 + 2H_2O,$$

with sulphur dioxide present in the sulphur in considerable quantities. The last two substances slowly interact at comparatively higher temperatures, giving rise to polythionic acids.

An attempt was made to investigate the action of anhydrous liquid hydrogen sulphide on liquid sulphur dioxide, but the drying of the gases was probably not thorough enough. About 5 c.c. of liquid hydrogen sulphide were collected in a thick-walled glass tube surrounded by a freezing mixture, dry sulphur dioxide passed in until the volume of the mixed liquids measured some 15 c.c., and the tube then sealed at the blowpipe. A slight yellow deposit was formed where the tube was sealed. After one day, a thin yellow film had formed at the upper part of the tube which gradually increased, and when the tube was opened after one week there was found in the bottom a solid lump of sulphur covered by a clear liquid. This liquid, when allowed to evaporate, gave off sulphur dioxide and left a small quantity of water containing dissolved sulphur dioxide.

Methods for the detection and estimation of the different polythionic acids which will, it is hoped, enable the composition of the oily mixture of acids to be accurately determined are at present being investigated.

R. CLAY AND SONS, LTD., BREAD ST. HILL, E.C., AND BUNGAY, SUFFOLK.

AN IMPROVED FORM OF APPARATUS FOR THE RAPID ESTIMATION OF SULPHATES AND SALTS OF BARIUM.

BY

WILLIAM ROBERT LANG

AND

THOS. BOLES ALLEN.

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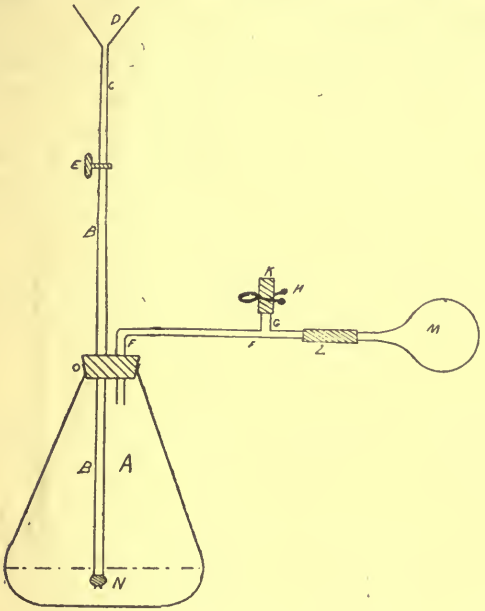
From the Transactions of the Chemical Society, 1907. Vol. 91.

CXXVII.—*An Improved Form of Apparatus for the Rapid Estimation of Sulphates and Salts of Barium.*

By William Robert Lang and Thos. Boles Allen.

N. Tarugi and G. Bianchi (*Gazzetta*, 1906, **36**, i, 347) describe an apparatus for the rapid and exact estimation of sulphates and salts of barium by a volumetric method based on the rapid clearing of turbid solutions in narrow tubes. (For a short description of their apparatus



see Abstr., 1906, **90**, ii, 627.) The authors have modified this apparatus materially; the following short description and diagram will serve to explain it.

The vessel, *A*, containing the acidified sulphate is placed on a flat burner, the approximate amount of barium chloride solution, ascertained by previous rough experiments, run directly into the flask, the stopper, *O*, with its attachments, inserted, and the contents kept at the boiling point. *FF* is a T-tube, on the branch, *G*, of which is fixed a small piece of rubber tubing with a pinchcock, at this stage of the experiment left open to the air. *N* is a small thistle-shaped tube filled with glass-wool which is found materially to clear the turbid solution as it passes up to the narrow tube. The pinchcock, *H*, is then

closed and a slight pressure on *M* forces a portion of the contents of the flask through *N* and up *B* until the portion *C* is filled, when the stopcock, *E*, is closed. The whole pressure on the flask can then be relieved by opening the pinchcock, *H*. The liquid in *C* clears very rapidly and the standard barium chloride solution may be added. If this produces a turbidity, *E* is opened and the solution washed down into the flask ; a very complete mixing is then obtained by alternately compressing *M*, with *G* open to the air, placing the finger on the orifice of the short rubber tube, *K*, and releasing *M*, thus causing air to be drawn through *N* and to bubble through the solution.

The process of forcing the liquid up the tube, titrating, washing it down again, and mixing is repeated until a further addition of barium chloride solution causes no turbidity. The mean between the number of c.c. used up to the point of having an evident turbidity and the quantity necessary to the point where none is perceptible is taken as the amount of barium chloride solution consumed in the precipitation of the sulphate. As the amounts of barium salt and sulphate in solution approximate to each other, so the rapidity of the clearing increases, and when the reaction has almost reached the end-point this clarification is very nearly instantaneous.

Experiments were undertaken in this apparatus with the solutions of sulphates and barium salts given in the following tables :

TABLE I.

Using 0·0958*N* – H_2SO_4, 1 c.c. = 0·0046 gram (SO_4).
„ 0·1101 *N* – $Ba(NO_3)_2$, 1 „ = 0·00485 „ (SO_4).

No. of c.c. of H_2SO_4 taken.	Equal to gram (SO_4).	No. of c.c. of $Ba(NO_3)_2$ taken.	Equal to gram (SO_4).	Error in per cent.
10·42	0·0479	10·00	0·0485	– 1·0
10·60	0 0488	10·00	0·0485	+ 0·6
10·52	0·0484	10·00	0·0485	– 0·2
10·58	0·0487	10·00	0·0485	+ 0·4
16·80	0·0773	16·00	0·0776	– 0·3
15·71	0·0722	15·00	0·0727	– 0·7

Average error – 0·55 and + 0·5, giving a mean error of 0·025 per cent.

TABLE II.

Using 0·9981 *N* – H_2SO_4, 1 c.c. = 0·0479 gram (SO_4).
„ 0·1101 *N* – $Ba(NO_3)_2$, 1 „ = 0·00485 „ (SO_4).

No. of c.c. of H_2SO_4 taken.	Equal to gram (SO_4).	No. of c.c. of $Ba(NO_3)_2$ taken.	Equal to gram (SO_4).	Error in per cent.
5·05	0·2419	50·00	0·2425	0·4
5·08	0·2433	50·00	0·2425	0·4
5·09	0·2438	50·00	0 2428	0·5
			Average error.....	0·43

TABLE III.

Using 0·2039 N – H_2SO_4, 1 c.c. = 0·0099 gram (SO_4).
„ 0·1101 N – $Ba(NO_3)_2$, 1 „ = 0·00485 „ (SO_4).

No. of c.c. of H_2SO_4 taken.	Equal to gram (SO_4).	No. of c.c. of $Ba(NO_3)_2$ taken.	Equal to gram (SO_4).	Error in per cent.
14·75	0·1460	29·95	0·1453	1·0
14·81	0·1466	30·00	0·1455	0·9
17·35	0·1717	34·90	0·1700	0·6
9·90	0·0980	20·10	0·0975	0·5
			Average error.....	0·75

Solutions of coloured sulphates, such as those of copper and nickel, were also tried, the error in these cases ranging from 0·1 to 0·8 per cent. of the theoretical.

From a study of these results it appears that a single titration will come within 1 per cent. of the value found by gravimetric estimation, and, if a sufficient number of titrations are made, the results can be obtained to within 0·5 per cent. of the gravimetric value (compare Table I.). It may be added that the presence of free acid materially aids the precipitation, greatly increasing the rate of precipitation of the turbid liquid in the narrow tube.

The determination of sulphur in iron pyrites by this method gave :

	Gravimetric.	*Volumetric.*
Iron salts present.....	52·13 per cent.	52·20 per cent.
Iron salts absent	52·24 „	52·09 „

It would seem that this method might be used in cases where speed is of more importance than absolute accuracy. It has this great advantage, that an estimation agreeing within 0·5 per cent. of the best gravimetric method can be made in from three-quarters to one hour ; that is, by taking the mean of four or five volumetric readings.

The Determination of Sucrose by Fehling's Solution.

Experiments with this apparatus were made to determine the best conditions under which the above could be most accurately carried out.

TABLE IV.

	No. of c.c. of sucrose taken.	Equal to gram sucrose.	Dilution in c.c.	Time of heating in minutes.	No. of c.c. of solution used.	Equal to gram sucrose.	Error in per cent.
(1)	10·00	0·2278	200	5	45·50	0·2275	0·2
(2)	10·00	0·2278	150	5	45·65	0·2283	0·3
(3)	5·00	0·1136	100	5	22·75	0·1138	0·2
(4)	10·00	0·2278	150	5	45·64	0·2282	0·2
(5)	10·01	0·2280	150	5	45·58	0·2279	0·1
(6)	10·00	0·2278	175	5	45·62	0·2281	0·1
(7)	10·00	0·2278	150	8	45·65	0·2283	0·3
(8)	2·00	0·0456	200	5	9·02	0·0451	1·0
(9)	5·00	0·1136	450	5	22·90	0·1145	1·0
(10)	10·00	0·2278	450	5	45·92	0·2296	0·9
(11)	10·00	0·2278	150	15	45·82	0·2292	1·0
(12)	5·00	0·1136	100	20	23·20	0·1160	2·0

These results are some of a number of determinations, and they show that, if suitable conditions are obtained, the results give excellent agreement with the theoretical. The conditions are, first, that the Fehling's solution should be added to the boiling liquid to within 1 c.c. of the correct amount, this being obtained by previous rough titrations; secondly, that the strength of the sucrose in the flask should not be more than 0·15 gram in from 75—100 c.c. of water, and thirdly, that the time of heating should not be more than from five to eight minutes.

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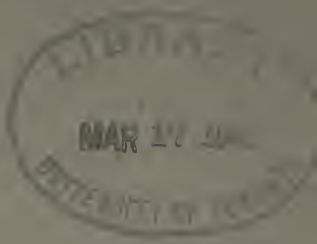

No. 46: THE ACTION OF LIQUEFIED AMMONIA ON CHROMIC CHLORIDE, BY W. R. LANG AND C. M. CARSON

NOTE ON THE ACTION OF METHYLAMINE ON CHROMIC CHLORIDE, BY W. R. LANG AND E. H. JOLLIFFE

(REPRINTED FROM THE JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, VOL. XXVI.)

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Vol. XXVI. No. 4. April, 1904.

THE ACTION OF LIQUEFIED AMMONIA ON CHROMIC CHLORIDE.

By W. R. Lang and C. M. Carson.

Received January 30, 1904.

Jörgensen describes a number of compounds derived from chromic chloride by the action on chromous chloride of aqueous ammonia, ammonium chloride and subsequent oxidation.

The authors have obtained similar substances by the direct action of dry liquid ammonia on violet chromic chloride at low temperatures. Violet chromic chloride is not acted upon by aqueous ammonia nor by dry ammonia gas, but liquid ammonia acts upon it readily, completely transforming it into a salmon-colored powder.

Experimental.—Three grams of powdered chromic chloride were placed in a vessel made of combustion tubing, closed at the lower end and drawn out at the neck to allow of the tube being sealed at the blowpipe. The whole was placed in a freezing-mixture, consisting of solid carbonic acid and ether, and ammonia, dried over potassium hydroxide, was passed in. No action took place until liquefaction began, when the chromic chloride swelled up and became pasty, the color changing at the same time to a dark salmon-pink. Ammonia in considerable excess was allowed to accumulate on the top of the mass and the tube was then sealed. The tube containing the salmon-colored material was set aside for a week at the room temperature, being shaken occasionallly to insure thorough mixing. Subsequent experiments showed the action of the ammonia to have been complete from the first, so in preparing further quantities this was omitted. The liquid ammonia on standing separated out colorless. The tube was then cooled to —35° and opened, the temperature raised gradually to 0°, at which it was kept constant for twenty-four hours, and the dry powder remaining kept for investigation. Further quantities were prepared in the same way and left standing at 0° for two and four days respectively. Another portion of the powder was left at 15° C. for two days, and yet another portion was heated to 110° C. for the same length of time when the color became more distinctly pink. Analyses of the powder obtained at 0°, 15°, and 110° respectively yielded:

	(A) At 0°. Per cent.	(B) At 15°. Per cent.	(C)[1] At 110°. Per cent.
Chromium	20.1	20.6	21.7
Chlorine	41.1	41.6	44.1
Ammonia	38.6	37.8	34.1
	99.8	100.0	99.9
Corresponding to molecules of NH_3 per molecule of Cr_2Cl_6	11.7	11.2	9.7

[1] This analysis was done by Mr. J. A. M. Dawson.

Further heating continued for twenty-four hours to 130° brought about the separation of a small amount of chromic oxide but complete decomposition into chromic oxide did not take place until a temperature of 180° was reached.

From the analytical results it was evident that the powders contained a mixture of substances, and the following investigation led to the isolation of two definite compounds therefrom.

I. The powder which had remained at 0° was treated with a small quantity of cold water, 5 cc. to every gram of the substance. Partial solution took place, and on filtering off from the undissolved solid, a clear solution of a brown color was obtained, which on standing in the air for even a short time, evolved ammonia and deposited chromium hydroxide. On removing the precipitated chromium hydroxide and rapidly evaporating *in vacuo,* yellow crystals separated out, which were collected and dried between filter-paper (for convenience let α indicate the yellow crystals). The residue from this first extraction with water was treated in the cold with a further quantity of the solvent and filtered. Evaporation *in vacuo* yielded, when carefully conducted, red crystals (β). When the concentration in the vacuum desiccator was conducted too slowly, slight decomposition into gelatinous chromium hydroxide took place with the evolution of ammonia, but if rapidly conducted in shallow evaporating dishes, the crystals separated readily from the solution and no ammonia was evolved. Analysis of the yellow compound and the red compound gave:

	α-Salt. Per cent.	β-Salt. Per cent.
Chromium	18.7	21.52
Chlorine	38.0	43.20
Ammonia	36.6	35.00
Water (by difference)	6.7	0.00
	100.00	99.72

The composition of the yellow α-compound thus corresponds with the formula $Cr_2Cl_6,12NH_3,2H_2O$, and that of the red β-compound with $Cr_2Cl_6,10NH_3$.

II. The powder obtained by keeping the original substance at 15° was similarly extracted with water, and from it were obtained yellow and red crystals, whose composition and properties were identical with the α- and β-compounds obtained in I.

III. Treatment of the original pink substance with cold water,

which had been maintained for two days at 100° C., yielded no α-crystals, but the red β-compound only.

PROPERTIES OF THE α-AND β-CRYSTALS.

The yellow crystals are soluble in water, but insoluble in hydrochloric acid and in alcohol. From the aqueous solution all the chlorine is precipitated in the cold by silver nitrate. On standing at 110° for two days, the yellow crystals are changed partly into a red powder, with separation of chromic oxide. These crystals evidently correspond with the *luteochromium* compounds obtained by Jörgensen[1] of the general formula $Cr_2 12NH_3X_6$.

The red compound crystallizes in small perfectly formed cubes and octahedra. They dissolve in cold water slowly, while hot water causes a separation of chromium hydroxide. Hydrochloric acid and alcohol exert no solvent action on them. Further, when the crystals are treated with liquid ammonia, no change takes place, and on addition of a small quantity of violet chromium chloride to the mixture of the salt and ammonia the chromic chloride reacts at once with the ammonia, yielding a pink powder from which the β-crystals may be separated mechanically. On treating the mixed crystals and powder with cold water, the latter readily dissolved away, leaving the red crystals untouched. The composition of this β-compound, $Cr_2 10NH_3Cl_6$, points to its being *chlorpurpureochromium chloride.*

CHEMICAL LABORATORY, UNIVERSITY OF TORONTO.

NOTE ON THE ACTION OF METHYLAMINE ON CHROMIC CHLORIDE.

BY W. R. LANG AND E. H. JOLLIFFE.

Received January 30, 1904.

A SOLUTION of methylamine was gently heated and the gas conducted through drying towers filled with potassium hydroxide to a glass tube containing chromium chloride and immersed in a freezing-mixture at a temperature of —10°. As soon as the liquid methylamine collected in the tube, combination between it and the chromic chloride took place and a substance of a pale pink color, closely resembling the ammonia compound (Lang and Carson), was formed. The excess of methylamine was allowed to pass off

[1] *J. prakt. Chem.*, [2] 30, 1.

and the contents of the tube dissolved in water. The substance was very soluble and the least possible quantity of water was used. The solution, on rapid evaporation *in vacuo*, yielded dark red crystals. Considerable difficulty was experienced in obtaining these crystals, owing to the rapidity with which the solution decomposed into chromic hydroxide; consequently the analysis of the crystals obtained by repeated operations had to be made on very small quantities. Analysis of the crystals thus obtained from the compound at a temperature of 15° gave:

	Found. Per cent.	Calculated for $Cr_2Cl_6.10CH_3NH_2$. Per cent.
Chromium	16.25	16.68
Chlorine	35.20	33.92
Methylamine	48.50	49.6
	99.95	100.00

Crystals produced in a similar manner from the original compound, previously heated to 94°, gave:

	Found. Per cent.	Calculated. Per cent.
Chromium	16.55	16.61
Chlorine	34.19	33.86
Methylamine	48.89	49.53
	99.63	100.00

The composition of these crystals is therefore $Cr_2Cl_6.10CH_3NH_2$, corresponding to the similarly constituted chloropurpureochromium chloride obtained (Lang and Carson) from anhydrous ammonia and chromic chloride.

On heating to 100° the compound formed by the direct action of methylamine on chromic chloride, analysis showed it to contain 43.26 per cent. of methylamine, which would point to its composition being Cr_2Cl_6, $8CH_3NH_2$, the percentage in this latter being 43.8. At 124° C. complete decomposition into Cr_2O_3 took place.

The analogy between the crystals thus obtained and the chloropurpureo compound is evident. The great difficulty of obtaining pure methylamine on the American continent prevented the investigation of these substances being continued further or more accurate analyses being made. Aniline and methylaniline had no action on the violet chromic chloride whether in the cold or when heated together. The effect of heating for any length of time in a sealed tube was not tried.

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No. 53: THE CHEMICAL INDUSTRIES OF THE DOMINION
BY W. R. LANG

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THE CHEMICAL INDUSTRIES OF THE DOMINION.

BY W. R. LANG, D.Sc.,

PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF TORONTO.

(*Read 10th December*, 1904).

(*Completed for publication, April*, 1905).

PREFACE.

MUCH of this paper appeared about two years ago in the *Journal of the Society of Chemical Industry*.* Recently it was communicated by request to the Canadian Institute after having been revised and, in a measure, brought up to date. A closer scrutiny of the subject matter, however, led to the conclusion that entire revisal and rewriting were necessary in order that it might present the condition of the chemical industries of the Dominion as they are at the time of publication. Every effort has been made to do this as far as possible, and the writer hopes that any shortcomings will be brought to his notice.

In writing on such a subject as the Chemical Industries of Canada, two main considerations have been kept in mind; firstly, that the development of the industrial resources of the Dominion during the past decade has been phenomenal, and secondly, that the extent of these developments is only fully understood by a few. While it is impossible to discuss *all* the industries in which chemical operations and reactions are made use of, an attempt has been made to select processes in some cases peculiar to the country, but notably the industries which owe their development to the natural mineral and vegetable resources, and to the widely scattered water power obtainable in the Dominion.

The subjects taken up may be classified as follows:—

I.—Common Salt and Alkali.
II.—The Extraction and Refining of Metals.
III.—The Manufacture of Leather.
IV—Sulphuric Acid, Acetic Acid, Wood Alcohol, Charcoal, and Ammonia
V.—Soap and Glycerine.
VI.—Refined Chemicals and Drugs.
VII.—Fertilizers.

* Journal of the Society of Chemical Industry, May 15th 1903

VIII.—Coal-Tar and Asphalt.
IX.—Calcium Carbide, Carborundum, Corundum and Graphite.
X.—The Cement and Plaster Industry.
XI.—The Beet-Sugar Industry.
XII.—Natural Gas and Petroleum.
XIII.—Pulp and Paper.
XIV.—Asbestos and Mica

I.—COMMON SALT, ALKALI AND CHLORINE COMPOUNDS.

Sodium chloride is found in the upper silurian beds in Ontario, and in the Devonian in Manitoba and Athabasca; salt springs also occur in Cape Breton and in New Brunswick, but these are comparatively unimportant sources of supply. In Ontario the salt area stretches through the counties of Middlesex, Huron, Bruce, and Lambton, large deposits being found along the shore of Lake Huron from Kincardine to Windsor. At Goderich there is a deposit 126 feet thick, and at Windsor a well extending to a depth of 1,672 feet passes through four beds of rock salt of an aggregate thickness of 392 feet.[1] The salt is obtained by evaporation, and is of an excellent quality. The following comparison serves to illustrate the purity of the natural product.[2]

	Natural Salt of Goderich, Ontario.	Natural Salt of Cheshire, (England.)
	Per Cent.	Per Cent.
Sodium chloride	99.687	96.70
Calcium chloride	0.032	0.68
Magnesium Chloride	0.095	0.00
Calcium sulphate	0.090	0.25
Moisture	0.079	0.63
Insoluble matter	0.017	1.74
	100.000	100.000
Total Impurities	0.234	2.67

The total production of salt in Canada was valued in 1892 at $162,000, in 1901 at $262,328, and in 1903 at $334,000.[3 *bis*.]

Apart from its use as a seasoning and as a preservative, common salt is employed in the electrolytic preparation of caustic soda and bleaching compounds.

The alkali and bleaching powder industries throughout the world

(1) W. Hodgson Ellis, M.B., in "A Handbook of Canada," 1897.
(2) Wilmott, A.B., "Some Minor Minerals of Canada," 1897.
(3 *bis*.) Statistical Year Book, 1903.

are at the present time in an unsettled condition, mainly owing to the advent of electrolytic methods.[3] Wherever cheap water power is available, however, electrolytic processes will be rapidly developed, provided the raw material is obtainable within a reasonable distance.

II.—THE EXTRACTION AND REFINING OF METALS.

Almost every province in the Dominion possesses valuable mineral resources; these are rapidly being exploited, and among the metals produced in quantity may be mentioned iron, copper, lead and silver, nickel, arsenic, antimony, and, lastly, aluminum. These metals are found in the form of native iron, magnetic iron ore, iron pyrites, hæmatite, native copper, chalcopyrite, galena, native silver and ores of silver, nickeliferous pyrrhotite, gold, sulphide of antimony, and arsenical pyrites.

IRON.

The iron ores of the Dominion occur at varied intervals, from Vancouver Island on the west to Cape Breton Island and Newfoundland on the east. In Nova Scotia there are particularly rich deposits, and in close contiguity to them are found the necessary materials for smelting. Hæmatites, too, are found in all parts of Canada. One of the most valuable deposits of specular iron is at Hull, near Ottawa, which assays from 64 to 68 per cent, of metallic iron. In the Appendix (Appendix I.) will be found more particulars regarding the iron ores of the Dominion.

The Canadian iron industry dates back to the establishment of the St. Maurice forges by the French Government in 1737. Many other minor plants were subsequently built, as at Batiscan, Hull, and Bois de Paul, all in Quebec; at Furnace Falls, Mormondale, Marmora, etc., in Ontario; at Woodstock, in New Brunswick; and at Moose River, Nictaux, and Bloomfield, in Nova Scotia. They all subsequently failed, however, in consequence of the competition of Great Britain and the United States. This early failure was due as much as anything else to lack of enterprise, capital, and proper shipping facilities. The modern development of the industry may be said to date from the introduction of a protective duty on iron in 1887. The granting of bounties by the Dominion and Ontario Governments has also assisted largely in bringing about the present condition of the iron and steel industries.[4] The annual aggregate capacity of the completed and unfinished furnaces in the Dominion in 1903 was

(3) Chem. Tr. J., 23.8.02, 6.9.02, and 24.1.03.

(4) Dominion bounty on pig iron, $3 per ton produced. Ontario bounty $1 per ton on pig iron produced from Ontario ores, and 50 cents on ores not obtained in the Province; the rate of $1 to be only paid up to 25,000 tons. Bounty is at present largely reduced owing to increased production.

close on 1,000,000 gross tons.[5] Much of the iron produced is now being made into steel[6] by the Bessemer process. At Sault Ste. Marie there is an extensive plant with a capacity of 200,000 tons of ingots and 180,000 tons of finished products. There, steel rails are being made to the extent of 500 tons a day. This company has its own blast furnaces, and undertakes all the processes, metallurgical and mechanical, through which the metal goes in its conversion from ore to finished product.

At Collingwood, Ontario, the Northern Iron and Steel Company, which recently acquired the works of the Cramp Steel Company, have two 20-ton open hearth furnaces besides rolling mills from which will be turned out material suitable for machinists' and blacksmiths' use, finished steel bars, angles, fish plates, tie plates and small sections such as are used by many manufacturers. The Gilchrist Thomas is the process employed, a process which allows of ores containing phosphorus, for example, to be profitably converted into good uniform steel. The ten inch mill at the Collingwood works is equipped with underground tunnels and turtle-backs for the purpose of continuous rolling, that is to say, a bar of steel will be looped from one pass of the rolls into another pass: thus a mill of this description is enabled to roll rods and long bars. The furnaces are of the latest standard design, having air cooled end blocks and slag pockets with the regenerators under the charging platform, which is of steel and concrete.[7] Recently the company has begun to convert, by "cold-drawing," steel bars into wire of various gauges.

The Canada Iron Furnace Company has its principal plant at Midland, Ontario, besides several other smaller establishments in various parts of Quebec. The Midland furnace was erected during 1899-1900 on a property about 100 acres in extent, situated on the north shore of the Midland Bay. The furnace proper has a capacity of from 120 to 140 tons a day of "Midland Brand" Foundry Malleable Bessemer and Bessemer Pig Iron, and is marketed almost entirely in Ontario. The raw materials used are coke, iron ores and limestone. The coke is obtained from the Connellsville district in Pennsylvania, and is brought in by rail. The iron ores are brought in by vessel from Canadian and United States ports on Lake Superior and also Lake Michigan. The limestone is obtained from the company's own quarry, which is about 130 acres in extent, situated about three milles from the furnace. This material is brought to the furnace by scows in the summer and by teams in the winter.[8]

(5) In a letter from Mr. T. W. Gibson, Director of the Ontario Bureau of Mines, the following figures are given for 1903:

Pig Iron produced in Ontario		87,004	tons.
Steel	" "	15,229	"
Pig Iron	" Canada	265,418	"
Steel	" "	232,641	"

(6) Dominion bounty on steel, $3 per ton; $2 per ton on steel from foreign ores.
(7) Letter from Mr. J. A. Currie.
(8) Letter from Mr. A. C. Adams, Midland.

On the eastern seaboard of the Dominion are situated the works of the Dominion Iron and Steel Company, begun in 1899. Coal and limestone are found comparatively near at hand, the farthest afield mine from which the coal supply is drawn being twenty-five miles distant, while the nearest one is six miles. Nearly all the iron ore at present used is brought from mines owned by the company on Great Belle Island in Conception Bay, Newfoundland, some 400 miles from Sydney. This mine is estimated to contain 28 million tons of available ore, besides areas under the sea, which are believed to be very extensive. Analyses of the ore show it to contain fifty per cent. of iron, little sulphur, but rather too much silica, aluminium, and phosphorus. The result is a pig iron too high in phosphorus, but during the subsequent conversion of the pig into steel in open-hearth furnaces, this impurity is eliminated, and a fine quality of steel produced. For the best kind of pig iron, it is necessary to mix other ores with it, and for this purpose Cuban, Spanish, and Swedish ores are used, the result being a low phosphorus pig. Indications of large deposits of high-grade ores have been found both in Nova Scotia and Cape Breton, which, when fully developed, will in a great measure replace the foreign ores.

Limestone is obtained from the company's quarries at the Bras d'Or Lakes, about eighty-five miles, by water, from the works. It is a stone of good quality, and is found in large deposits; it acts well with the Newfoundland ore and the Cape Breton coke[8 *bis*.] The works contain four blast-furnaces capable of yielding 1,000 tons of pig iron per day; the furnace gases are utilized also to the utmost, being used to heat the blast and also to raise steam. The iron produced is partly cast into pigs and in part conveyed in a molten condition direct to the open-hearth furnaces, where it is converted into steel. Of these there are ten in number of the H. H. Campbell type of tilting basic open-hearth furnaces, having a capacity of fifty tons each. A very complete arrangement of testing the steel at intervals is in vogue, and of stamping each ingot with special marks so that the consumer can ascertain from the company at any time every particular regarding the analysis and making of the piece.

The gases produced in the coke ovens are used in the opening hearth furnaces, the other bye-products, namely, coal-tar and ammonia, being also collected. The ammonia is converted into sulphate of ammonium by neutralizing it with sulphuric acid—which can be obtained from the pyrites separated from the coal in the preliminary grinding and washing processes to which it is subjected, and is principally exported to the United States, the West Indies, and Glasgow.

(8 *bis*.) The daily shipment is 1,500 tons.

Canadian-made steel is largely exported to the United States from where it returns to this country in the form of rails and other finished products; but it is intended that this feature of the steel industry will shortly be transferred to Canadian territory. Sydney is extremely well situated as a seaport, being nearer to England than is New York, and, strange as it may appear, to the ports of South America and South Africa.[9] As far as the geographical position is concerned, therefore, Sydney possesses many advantages, while the masterly and liberal way in which the iron and steel industry has been organized and developed, points to a bright future for it in Canada.[10]

A new plant has been erected near North Sydney by the Nova Scotia Steel Company, who have at present works at Ferrona, with a limited supply of ore near at hand. Hence they import largely from Newfoundland. Their steel works are at present at New Glasgow, but a new plant is under construction at Sydney (1903), Their output, which is sold almost exclusively in Canada, approximates 100 tons of pig-iron per day and the same amount of steel.[10 *bis*.]

COPPER.

The production of refined copper can hardly be classed among the chemical industries of the Dominion, as practically only the first stage in its extraction of the metal is reached, namely, the making of copper matte, which is exported to the United States to be refined. As will be seen below, however, the refining of this metal is now being carried on in British Columbia.

Copper ores occur in great abundance, and constitute one of the most important mineral resources of the country. These are distributed over large tracts in Ontario, Quebec, Nova Scotia, and New Brunswick. The deposits consist of native copper and sulphides, the former confined principally to the Lake Superior region, the latter being more widely diffused,

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	Miles.
(9) Sydney Harbour to Liverpool (*via* South of Ireland)	2,307
New York Harbour to Liverpool	3,110
Sydney Harbour to Pernambuco	3,567
New York Harbour to Pernambuco	3,696
Sydney Harbour to Cape Town	6,467
New York Harbour to Cape Town	6,787

These figures were supplied to me by Mr. Watson Griffin, who obtained them from Captain W. H. Smith, R.N.R., Halifax. The distances from New York were compiled by the United States Commission of Navigation.

(10) Mr. Watson Griffin, who kindly supplied me with material from which the above description of the Sydney operations was written, mentioned also that a leading Scottish iron and steel magnate told him that, everything considered, Sydney, in regard to raw materials, nearness to the mark and the excellent equipment it possessed, would be the finest steel manufactory in the world. Watson Griffin, "Dominion Steel and Coal Co., Sydney;" Montreal, 1902. Watson Griffin, "The Front Door of Canada;" Montreal, 1899.

(10 *bis*.) The production of pig iron in 1903 amounted to 265,418 tons, as compared to 47,000 tons in 1893, while the proportion of the home product to the total consumption of pig was 76 per cent. in 1903 as compared with 42 per cent. in 1893.

but notably in the Sudbury region, Ontario, where it occurs with nickel. The production of copper, other than the native copper near Lake Superior, is dependent for the most part on that of this latter metal.

The British Columbia Copper Company is now turning out about seven million (7,000,000) pounds of copper a year and has an excellent converter plant at its mine. This copper is produced at a cost of about 9½ cents a pound. The product from the converter is blister copper and is sent to New York to the Nicholls Chemical Company to be refined. The Montreal and Boston Copper Company is now producing about 3,000,000 pounds of copper and is selling its matte to the British Columbia Company. The Granby Company is producing about 15,000,000 pounds of copper a year, at a cost of around 9½ cents, laid down in new York.[11]

Some idea of the advances made in the production of copper matte may be had from the fact that in 1893 the production amounted to 8,000,000 pounds, while 1903 showed an output of 43,000,000 pounds.[11 *bis*.]

Mr. A. P. Turner of the Canadian Copper Company at Copper Cliff, Ontario, has furnished some interesting particulars regarding the production of copper as carried on at the works of this company, which controls about 20,000 acres of mineral lands in the nickel district extending from Garson Township in the District of Nipissing, south-west to Drury Township in the District of Algoma, in the Province of Ontario. The company began operations in 1887, and at present is mining and smelting about 700 tons of ore per day. The ore is a mixture of nickeliferous pyrrhotite, pentlandite, chalcopyrite and diorite. The nickel in this pyrrhotite replaces about two to four per cent. of the iron. Copper occurs in the form of copper pyrites. The ore contains no arsenic or antimony, but small traces of gold, platinum and palladium. An average assay of the different mines is about two per cent. copper and four per cent. nickel.

The company has designed and just finished at Copper Cliff, a new smelting and power plant, in which are combined the latest and best improvements in the smelting world. There are larger plants, but it is doubtful if there is another in which are assembled so many up-to-date conveniences for every part of the work.

NICKEL.

The first discovery of nickeliferous deposits was made in 1883 near Sudbury, in the district of Algoma, Ontario. Previous to the discovery of nickel in this country, the French colony at New Caledonia practically

(11) Letter from Mr. F. P. Clappison.
(11 *bis*.) Statistical Year Book, 1903.

contributed the world's supply of the metal, though supplemented, in a small degree, by the Gap Mine in Pennsylvania, and by a few isolated mines in Norway and Hungary. Professor Coleman[12] states that the Sudbury ores consist of a mixture of pyrrhotite (magnetic pyrites) and copper pyrites, and in this resemble the gold ores of Rossland. In order to obtain the metal the ore is smelted into a matte, containing from twelve to twenty per cent. of nickel and about the same amount of copper, is "Bessemerized" into a regulus containing about forty per cent. of nickel and is shipped to Clydach in Wales, where its nickel content is extracted and refined by the process invented by Dr. Ludwig Mond, F.R.S., and which bears his name. The chemical principle on which this process is based is the formation, at temperatures of about 50° C., of a volatile colourless gaseous compound of nickel and carbon monoxide of composition Ni_4CO, which, on being subjected to a temperature of 180° C., decomposes, leaving metallic nickel and liberating the carbon monoxide. The product thus obtained contains between 99.4 and 99.8 per cent. of nickel. The Mond Nickel Company is the only company refining nickel within the British Empire, and it is interesting to note that at the recent St. Louis Exhibition Dr. Mond was awarded the gold medal for his process, the company receiving a similar honour struck in silver.[13] Nickel from Canadian ores is now being used in the manufacture of armour plate in constructing ships for His Majesty's navy.

What is known as the Orford or alkaline sulphide process of refining nickel is the one by which the Canadian Copper Company's mattes are treated at Constable Hook, N.J., by the Orford Copper Company. As this company (now forming part of the International Nickel Company) is the chief producer, the bulk of the nickel ores of Ontario are refined by the Orford process. An electrolytic refinery erected by the Canadian Copper Company at Cleveland, Ohio, was operated for a short time only, but shut down in 1902.[14]

The Orford Copper Company is also producing *palladium*. This metal belongs to the platinum group, and is found associated with it. The Sudbury ores are said to contain from one tenth of an ounce to one ounce per ton, and Dr. Joseph Wharton, in an article recently published [14 *bis*.] prophesies a future production of palladium from these deposits. Palladium is an interesting metal, not only from the chemist's point of view, but also from an industrial one, as its physical properties, hardness, etc., and the difficulty with which it is attacked and tarnished at atmos-

(12) 8th Report of Bureau of Mines, Ontario, page 106.

(13) A full account of the Mond Nickel Process will be found in the 8th Report, Bureau of Mines, Ontario.

(14) Letter from Mr. T. W. Gibson, Director of the Bureau of Mines, Ont.

(14 *bis*.) "Hardware and Metal," Dec. 3rd, 1904.

pheric temperatures, render it eminently suitable for replacing silver as a reflecting surface on optical instruments, for plating the finely cut scales on instruments of precision and for alloys.

ALUMINUM.

The extraction and refining of aluminum has in recent years, owing to the advent of electricity developed from cheap water power, become an important industry. At Shawinigan Falls, Quebec, are situated the Canadian works of the Northern Aluminium Company, a sub-company of the Pittsburgh Reduction Company, which also has two large factories at Niagara Falls, N.Y. The raw material, bauxite, is obtained from Alabama, Arkansas and Georgia, in the United States. The process employed is the Hall[15] process, and is a combined electrolytic and electric furnace one. The native aluminum hydroxide is first purified by mixing with sufficient carbon to reduce all impurities in it to the metallic state, the resulting iron, mixed with titanium and silicon, forming a slag after melting the mass in an electric furnace. An alternating current of low voltage is used, and the purified alumina separates out above the slag in an almost chemically pure condition. The alumina thus purified is then electrolyzed in a bath containing cryolite at a temperature of from 850° to 900° C. The action of the current sets free aluminum and oxygen, the latter uniting with the carbon anodes to form carbonic oxide. The metal is run into rough ingots weighing twenty pounds each, and is stated to contain, on an average, 99.5 per cent. of aluminum.[16] The principal portion of the product at Shawinigan is shipped in the form of ingots, although there is in addition a wire mill where aluminum wire and cable for electrical conductors are made.

The production of the Quebec works is probably 9,500 pounds per day, the value in 1902 being approximately $1,043,250.[17] It may safely be said that the three works of this company between them produce one-half of the world's supply.

LEAD AND SILVER.

These metals are derived principally from the mines of British Columbia, but there are also deposits of galena along the shores of Lake Superior, the ore from which is sent to Niagara Falls, N.Y., for reduction. The British Columbia ore is a high grade one, carrying from 25 to 300 ounces of silver to the ton. At Trail, in British Columbia, the Canadian Smelt-

(15) Dr. J. W. Richards in "Electro-Chemical Industry," Oct., 1902.
(16) *Ibid.* (average value of product is 31 cents per pound).
(17) Canadian Mining Rev., March, 1903.

ing Works have recently begun to produce commercial lead, stated to be of 99.9 per cent. purity,[18] by means of the Bett's process, which is an electrolytic one.

The Hall Mining and Smelting Works, whose Canadian headquarters are at Nelson, British Columbia, are smelting lead ores which are obtained in the Slocan and Kootenay Lakes. They employ blast furnaces, a considerable portion of the ore being first roasted in hand or mechanical furnaces, and the product of the latter briquetted. The principal markets for the pig lead are the Orient, England, and Canada, though the home market is somewhat handicapped by the present arrangement of duties, which allows the importation of foreign corroded lead at a lower rate than that imposed on pig-lead. With a revisal of the duties a greatly increased development and revival of the lead and smelting industries is anticipated.[19] *bis.*

In 1894 the amount of silver exported, in ores, concentrates, or otherwise, was 629,655 ounces, while in 1901 the quantity had risen to over 4,000,000 ounces.[19] Despite these figures, the *Monetary Times*, Toronto, of date January 16th, 1903, says, "The silver-lead production of British Columbia is severely handicapped by the adverse competition of the United States, the European and Mexican products. The tariff is unfavourable; a higher one would be quite beneficial to the industry."

During the session of 1903 the Parliament of Canada provided for the payment of a bounty of 75c. per hundred pounds on lead smelted in Canada from Canadian ores, the maximum amount of bounty payable in any one year being $500,000, and the rate subject to proportionate reduction when the standard price of pig lead in London, England, exceeds £12 10s. per ton of 2,240 pounds. This provision has led to the revival of silver-lead mining in British Columbia. A small plant for smelting lead has been erected at Bannockburn, Ont., to be used on the non-argentiferous ores of that locality.[19 *bis.*]

ARSENIC.

A not unimportent metal found in considerable quantities in Ontario is arsenic; the chief form in which it occurs is arsenical pyrites (mispickel), which also contains gold. Its manufacture was begun by the Canadian Goldfields, Limited, at their Delora Mine, Hastings County, Ontario, in 1899. Attempts had been made, extending over the previous twenty years or so, to extract the gold from the ore found there, and, after the mine had experienced some vicissitudes, the present company acquired

(18) Letter from the Business Manager, Hall Mining and Smelting Co., Nelson, B.C.
(19) Statistical Year Book of Canada, 1901.
(19 *bis.*) Letter from Mr. T. W. Gibson.

it and obtained the rights (1896) for Ontario to the Sulman-Tweed patents (bromo-cyanide process), working it with only a modified degree of success for a couple of years, when the installation of improved machinery and the adoption of a combination of amalgamation and leaching with bromo-cyanide resulted in the recovery of arsenic from the mispickel concentrates. To accomplish this the concentrates are heated to a high temperature in specially constructed cylindrical revolving calciners, and the resulting impure arsenious oxide evolved is condensed in hermetically sealed brick chambers.[20] The crude arsenic is refined by sublimation, and contains from 99.6 to 100 per cent. arsenious oxide, the main impurity being silica in a finely divided condition.[21] It is exported chiefly to the United States, where it is used for making "Paris Green," etc. The output has increased from 113,477 pounds in 1899 to 1,347,000 pounds in 1901.[21] In time and with proper development Ontario should be able to supply the entire demand for arsenic on the continent of America.

Auriferous mispickel mines are being opened up at Lake Temagami, and concentrating works are in course of erection. The process of refining the arsenic will be an electrical one. The ores of the Haileybury region, not far distant, discovered last year, contain 60 or 65 per cent. of arsenic, but are more valuable for their other constituents, including silver, cobalt and nickel.[19] *bis*.

ANTIMONY.

This metal might almost be said to occupy the position of a bye-product in the extraction of gold. At Rawdon, in Nova Scotia, the ore (stibnite) is auriferous, and from 1898 to 1901 no refined antimony was produced, the stibnite being mined for the sake of its more precious contents[22]. It is also found in Quebec, and recent reports indicate deposits of ore in several localities of Ontario and British Columbia. The output in 1891 had fallen to $60. In 1902 the refining of the metal was renewed.

GOLD.

Gold is mined to a small extent in Ontario, in Nova Scotia and Quebec. Gold deposits are also found in the Kootenay district, B.C., in Cariboo, B.C., and in the Yukon. In the Rossland district the ore is a cupriferous pyrrhotite under a diorite cap, and from Trail on the Columbia River, where the

(20) C. Kirkegaard, in Eng. and Mining J., Jan. 31, 1903.

(21) Bureau of Mines Report, Ontario, 1901.

(22) Assays of two ores give, according to the Nova Scotia Mines Report, 1901:—

	I. Per cent.	II. Per cent.
Antimony	45.75	18.21
Gold (oz. per ton)	2.48	0.23
Silver (oz. per ton)	0.10	0.13

ore is smelted, the gold-copper matte produced is shipped to Montana for refining purposes. There is also a smelter at Nelson for the ore of the Hall mine. The Yukon territory covers in a general way the district north of Cariboo, south of the Arctic Ocean, and lying between the Mackenzie River and the Alaska-Canada boundary. Gold has been known to exist there since 1864, and has been worked intermittently since 1873. Forty Mile River, a tributary of the Yukon, was discovered to carry coarse gold in 1886, and ten years later, what is known as the Klondike, was found to contain gold also, It was first discovered on Bonanza and Eldorado creeks;[23] the news of this discovery spread far and wide, and active prospecting was the result. There are about 1,400 miles of Canadian Yukon streams, on all of which gold can be found. Mr. Ogilvie, former Canadian commissioner in the Yukon, estimates that an area of 125,000 square miles is gold bearing.[24] The former difficulties of reaching the Yukon have now been overcome; a telegraph line has also been laid by the Canadian Government from Skagway, on the coast, to Dawson. The gold is found and worked in the gravel deposits of the valleys and on their adjacent slopes, and it has been estimated that gold to the value of 95,000,000 dols. will be produced from these deposits in the next few years.[25]

The gold fields of Nova Scotia occupy the entire Atlantic coast line, and contain gold in combination with sulphides and arsenides of iron, but mostly in the free state. The following table will best convey the output of gold from Canada and its distribution.[26]

	1892	1901
	Dols.	Dols.
Ontario	7,118	243,022
Saskatchewan, N.W.T.	98,006	15,000
Yukon	.....	12,500,000[27]
Quebec	12,887	3,000
British Columbia	399,525	5,596,700
Nova Scotia	389,965	604,500
Total	907,601	18,962,222

The gold production for the Yukon in 1902 was 12,018,561 dols.; according to the United States Mints it was 14,525,275.[28]

The total output of gold in Canada in the years 1893, 1900 and 1903 amounted respectively to $976,603, $27,908,153, and $18,834,373. The figures for 1904 are not yet available.

(23) "Official Guide to the Klondike," by William Ogilvie.
(24) *Ibid.*
(25) Report of the Canadian Commission in the Yukon.
(26) Statistical Year Books, 1892-1902.
(27) Letters from Mr. B. E. Walker, General Manager, the Canadian Bank of Commerce.
(28) Letter from Hon. Clifford Sifton, Minister of Interior, Ottawa.

III.—THE MANUFACTURE OF LEATHER.

The manufacture of leather has, during the last thirty years, occupied quite a prominent position in Ontario and Quebec, and, during the past few years, through the stimulus from a larger home market and increasing sales to foreign markets, has grown greatly. As compared with a decade ago the value of the leather produced in the country may safely be said to have doubled. There are from eighteen to twenty large establishments in operation and fully fifty small ones. No tanning is done in the North-West Territories, and practically none in British Columbia. Bark, chrome, and combination tanning methods are employed, the spent bark being utilized in large establishments in specially constructed furnaces. Though the United States may be said to lead the world in the extent of leather produced, the qualitv of the Canadian product is not surpassed. The Canadian specialties are hemlock sole and harness, black and coloured shoe leathers, coloured and fancy side leathers for the bag, trunk and saddle trades. In Toronto there are several sheep-skin tanneries as well.

Speaking generally Quebec supplies the cheapest grades of leathers, chiefly black; Ontario the better finished lines both black and coloured. A portion of the American patterned machinery employed and formerly imported is now being manufactured in the Dominion, such as bark mills, fleshing machines, glazing jacks, drums and presses; but the most expensive and elaborate machinery is still made in the United States. The import duty on machinery is 25 per cent. The manufacture of hemlock extract in New Brunswick has already had a beginning, and will doubtless grow as the prices of bark and labour advance.

IV.—SULPHURIC ACID, ACETIC ACID, WOOD ALCOHOL, CHARCOAL AND AMMONIA.

The manufacture of commercial sulphuric acid has not yet been developed to the extent that the quantity of sulphur found throughout the Dominion would justify. There is enough sulphur in Canada to supply the entire home market with acid and even to develop a considerable export trade. Only a few firms, however, are engaged in the trade, and a large portion of their product is used in the refining of Canadian petroleum, some five million pounds being annually consumed for this purpose. Quebec, Ontario, and British Columbia are each represented in the acid industry. It is probable that the construction of electrolytic lead smelters will lead to the sulphur dioxide obtained from the galena being made into sulphuric acid, as is done at the Electric Lead Reduction Company's works at Niagara Falls, N.Y., where, it is stated, the sulphuric acid produced

yields a financial return sufficient to cover the entire cost of the process.

At London, Ontario, the Canada Chemical Manufacturing Company turns out about fifteen tons of sulphuric acid per day; brimstone, imported from the States, is used, and is preferred to the Sicilian sulphur. This company does not use pyrites on account of the arsenic it contains. The process employed is the chamber one, indeed, as far as the writer knows, the "contact" process has not yet been tried in Canada. Sulphuric acid is used by many manufacturers, such as tack, screw, nail, leather and fertilizer makers, wholesale druggists, dyers and oil-refiners. Phosphates of calcium and sodium are also made by this company, native phosphates and the animal charcoal (bone black) rejected by sugar refiners serving as sources of phosphorus. The acid phosphate of calcium is employed in the baking-powder trade instead of cream of tartar, and is claimed to be less costly, to keep better, and to restore to the flour the phosphates which, by the modern methods of milling, have been removed from the wheat.

Sulphites, bisulphites, crude acetic acid from the grey acetate of lime, chlorides of zinc and iron and Glauber's salts are likewise made.

By the destructiye distillation of wood, acetic acid, wood alcohol and charcoal are obtained; hence Canada, with its enormous supply of wood of all kinds, should be able to take a prominent place in the production of acetic acid and wood spirit. At the present time the residual charcoal from the retorts does not find a ready market, owing to the comparatively high rates for transport as compared with other fuels, weight for weight. The outlook in this direction is, however, brightening. Among the firms engaged in this manufacture might be mentioned the Standard Chemical Company, with plants at Fenelon Falls, Deseronto and Longford, Ontario, and Copkshire, Quebec; the Canada Paint Company, Montreal and Toronto; and the Lake Superior Power Company, which is said to have the largest retort plant in the world. Very keen competition has to be faced in this connection with the United States, as a combination of some 175 manufacturers practically controls the market. The crude acetate of lime produced in the distillation process is converted into acetic acid, some of which is sold for dye and colour-making purposes, while a considerable portion is exported to Europe and Australia.

The wood alcohol, obtained at the same time as the acetic acid, supplies the home market and is also exported largely to Great Britain, France, Germany, Holland, Japan, and Australia. It may be of interest to know that timber is imported from Canada by makers of wood alcohol in the United States.[29]

(29) Mr. Webster, of the Standard Chemical Co.

The total production of ammonia from all the gas liquors obtained in the destructive distillation of coal throughout the Dominion is, the writer is informed by Mr. J. G. Harvey of Toronto, about 235,000 pounds of a 28° Beaumé solution. As this quantity is in excess of what is required to supply the Canadian market by some 100,000 pounds, that amount is exported to the States. Besides the numerous trade preparations of ammonia used for household and other purposes, "aqua ammonia" and anhydrous liquid ammonia are the two principal forms in which it is prepared. The process consists in mixing milk-of-lime in suitably constructed vessels with the ammoniacal gas liquor, agitating and heating with steam and conducting the liberated ammonia through more milk-of-lime, through a drip-tank and, in succession, through oil, charcoal purifiers, caustic alkali and finally to tanks of distilled water kept cool by running water, where the gas is absorbed and the ammonia of commerce thus obtained. Manufacturers claim that the amount of water required to be used during the process reduces the profits considerably, as the gas-liquors are of a poor quality, seldom exceeding 1½° Twaddle. Anhydrous ammonia is produced from the "aqua ammonia" by a series of fractional distillations, is liquefied by pressure and stored in hundred pound welded iron cylinders. It contains 99 per cent. liquid NH^3, and finds its principal use as a refrigerant.

V.—SOAP AND GLYCERINE.

SOAP.

The soap industry in Canada is growing rapidly; at the present time some fifteen large concerns are in operation, employing in all about 2,000 hands. A branch of the well-known firm whose headquarters are at Port Sunlight near Liverpool, was recently started in Toronto, with an annual capacity of 10,000 tons. Their products are similar to those made at their other works, and their raw materials are procured from Africa, the United States, and locally (tallow). They own islands in the Pacific from which they import cocoanut oil.

Many other firms are also manufacturers on a large scale and produce all grades, from the cheapest textile and laundry soaps to the finer qualities of toilet soaps. Great advances have taken place in the industry during the past ten years, particularly in the making of the latter. The same system of manufacture obtains in England. The raw materials are mainly cocoanut oil, palm oil, and tallow, the first two in a large measure superseding the last mentioned. The market for Canadian made soap is limited, the home market is supplied and a large export trade is done with the West Indies and Australia. The competition of the United States is felt more

than that of England or France. In 1902 the value of the soap produced was approximately $3,000,000.[30]

GLYCERINE.

This necessary bye-product in the manufacture of soap is refined in some cases by the producers themselves; others sell it to firms engaged more particularly in the refining trade. Among these might be mentioned the St. Henri Chemical Company, of Montreal, who buy waste lyes from the soap manufacturers, recover the salt from the lye, refine the glycerine, and sell to the makers of nitro-glycerine. The capacity of these works is 10,000,000 pounds of waste lye yearly.[31]

VI.—REFINED CHEMICALS AND DRUGS.

There are very few makers of refined chemicals in the Dominion. The small demand for pure chemicals is mainly accountable for the lack of local manufacturers, the market being necessarily a small one, and most buyers of pure chemicals for laboratory uses are apt to demand articles of the make of one or other of the large and old established German or English houses. One can hardly doubt but that the Canadian maker must desire a higher tariff on imported material. Of heavier chemicals, however, the Canadian Process Co. has recently begun the manufacture and the work is proving very successful. Such products are bisulphite, sulphide, thiosulphate (hyposulphite), sulphite and sulphate of soda, lime, and zinc salts, lactic acid, casein, etc. Messrs. Lyman Bros. and Company are continuing to extend along the lines of refined chemicals, their gold and silver salts being much in demand. Along with these they produce and refine such high grade chemicals as chloroform, ether, iodide of potassium, bromides, scale preparations, iron and zinc salts, acids of phosphorus, syrups, tinctures, and flavouring extracts. Most of the raw materials are imported. In the drug department this firm has probably the best grinding machinery in Canada, where, besides their own work, they do a considerable amount of grinding for other firms. In the strictly pharmaceutical business, Messrs. Parke, Davis and Company, Walkerville; H. K. Wampole, Toronto; F. Stearns, Windsor; and John Wyeth and Bro., Montreal, have manufacturing establishments. Recently the brand "Made in Canada" has been much in evidence, and many buyers prefer such goods, even if they are slightly more expensive, to the imported article.

A few years ago the Liquid Carbonate Company of Toronto commenced the manufacture of carbon dioxide on a commercial scale, and is now

(30) Mr. Knight, of the Sunlight Soap Co.
(31) Letter from the President of the Company.

producing some two tons a day. The methods employed for obtaining the gas are from the action of an acid, such as sulphuric acid, on chalk, dolomite or sodium carbonate, and by the combustion of coke, while it is also got as a bye-product from the fermentation vats in breweries. The gas, after being washed and purified, is compressed, cooled, and in liquid form is forced into steel cylinders at a pressure of from sixty to eighty atmospheres. (The cylinders are tested to a pressure of over two hundred atmospheres). This liquid gas finds a market from the Atlantic to the Pacific, and is used for aerating mineral and artificial waters, for forcing beer from barrels in the cellar to a higher level, and at the same time preserving it from deterioration. It is also used in the refining of sugar, as a motive power in spraying trees with a germicidal solution, and in the laboratory for producing low temperature mixtures. Numerous useful bye-products are a consequence of the process of production of carbonic acid, such as fine clay used by paper-makers, Epsom salts and Glauber's salts—all of which are employed in many industries and command a ready sale.

VII.—FERTILIZERS.

Mineral phosphates, in the form of apatite, are found in the Ottawa Valley, Ontario, but the deposits have not been worked for several years. About 1891, in which year the phosphates mined were valued at $50,000, a falling off began in the output of this mineral, which continued up to 1902, when the amount mined was hardly worth recording. This industry is on the increase again, however, and last year saw a production valued at some $8,000. This state of affairs has been brought about mainly by the large supply of easily-worked phosphates found in Florida and Carolina, U.S.A., much of which is obtained by dredging. It may be mentioned, however, that a certain amount of apatite is made use of in the Province of Quebec by the Buckingham Electric Reduction Company, who manufacture phosphorus therefrom.[32]

Sulphate of ammonia is manufactured at the works of the Dominion Iron and Steel Company, Sydney, N.S., whose products are supplied to dealers and others engaged in the fertilizer business. The ammoniacal liquors of the Quebec, Ottawa and Toronto Gasworks are worked up at the latter city by the Michigan Ammonia Company.[33] In Montreal, one firm at least, makes sulphate of ammonia, and at one time the gas works there utilized their own liquors for its production. Latterly, however, the gas liquor was exported, to be dealt with by a firm in the United States.

Quite a number of other fertilizers are produced in the Dominion from

(32) Minerals of Quebec: published by the Provincial Government.
(33) Letter from Mr. Macfarlane, Chief Analyst to the Inland Revenue Department.

refuse matter, such as blood, tankage, bones, and offal, besides natural phosphates. Ontario, New Brunswick, Quebec, Nova Scotia, Prince Edward Island, and British Columbia, all produce fertilizers, more or less.[34]

VIII.—COAL-TAR AND ASPHALT.

Very little tar distillation is carried on in the Dominion, owing mainly to the tar produced in the gasworks being too thick for treatment with any degree of success. It is mainly used for saturating paper, which is employed largely as a waterproofing material by builders. Some is boiled down into pitch, but about one half of the tar produced is exported to the United States. There is a small distilling plant at Hamilton, Ontario, which the writer understands, was, up to eighteen months ago, the only one of its kind from which coal-tar oils were produced in Canada. The Dominion Iron and Steel Company at Sydney obtain a considerable quantity of coal tar from their coke-ovens. This, at one time, found a market in the States, in Montreal and other points in Canada, but recently arrangements were made w th an English chemical company to locate at Sydney with a view to utilizing all the coal-tar produced from the coke-ovens. The works, which are one of the largest on the continent, are now in operation and doing a large business in Canada, Europe and the United States; the demand for the company's products in Canada is not sufficient, hence the European and American exports. The present products are pitch and the various grades of benzol, creosote-oil and carbolic acid.[35] Large extensions are looked for from this company, which will be guided by the motto *festina lente*, and as opportunity offers, will branch into the production of other commercial commodities arising out of coal-tar and its distillation products.

ASPHALT.

Asphalt occurs naturally in several varieties as albertite, found in King's and Albert Counties, N.B., and as maltha, one of the stiffer petroleum compounds, which is not of much importance however, being almost too hard for use in street paving. Up to 1898, albertite was employed in gas-making, and much of it was shipped to the United states; but the original supply is now exhausted.

IX.—CALCIUM CARBIDE, CARBORUNDUM, CORUNDUM, AND GRAPHITE.

CALCIUM CARBIDE.

The production of this substance on a manufacturing scale dates back only to the year 1891, when Mr. T. L. Willson, of the Willson Aluminum

(34) Inland Revenue Bulletin, No. 81, 1902.
(35) Letter from Mr. John Craven, Sydney, 2nd Feb., 1905.

Works, at Spray, N.C., accidentally obtained carbide whilst trying to reduce lime by carbon in the electric furnace. Instead of metallic calcium resulting—which was to be employed in preparing aluminum—a hard, almost black, substance was got which reacted violently with water, giving lime and an inflammable gas clearly recognizable as acetylene. The author was privileged, through the courtesy of Lord Kelvin, to have at one time in his possession some pieces of the first carbide made by Mr. Willson at Spray. Acetylene being a powerful illuminating agent and readily obtained from carbide, the development of the carbide industry on a commercial scale followed this discovery as a natural consequence. The industry has progressed by leaps and bounds during the past decade, in Europe even to the extent of over-production.[36] Two carbide works are in operation in Canada using water as their source of power, the Ottawa Carbide Company, and another important company is the Shawinigan Carbide Company of Shawinigan Falls, Quebec. The process of manufacturing consists in fusing together burned lime and ground coke in the electric furnace; the temperature required is not so high as that needed in other operations for which the electric furnace is employed, notably the making of carborundum and graphite. The reaction taking place in the furnace results in a transference of the oxygen of the lime to a portion of the carbon with the formation of carbon monoxide and carbide of calcium.

The present market value of carbide affords considerable profit to its manufacturers, and the increasing popularity of acetylene as an illuminant ensures a brighter future for the industry. In Ontario several towns have already had acetylene installed for house and street lighting, the gas being generated at a central station and distributed in pipes to the consumers.[37] At the generating station the gas is purified by a special process before use, which obviates all the disadvantages inseparable from the employment of small generators—automatic or otherwise—by individuals, who in most cases have neither the time nor the scientific skill necessary for the proper production of the gas, simple as it may appear at first sight.

CARBORUNDUM.

Ten years ago the very name "carborundum" was unknown; it is due entirely to the advance made in the development of electrical power, obtained from the immense waterfalls of the American continent, that this as well as other materials are now in daily use throughout the world.

(36) Italy alone possesses enough carbide plants to supply the whole of Europe. Dr. J. W Richards, in "Electro-chemical Industry," Sept. 1902.

(37) Worked under patents held by the Burgess Gas Process Co., Canadian Pat. 73,040 Sept. 10 1901; Eng. Pat. 241, Jan. 3, 1901; Amer. Pat. 701,995, June 10, 1902.

The history of carborundum, may well be likened to that of carbide, its discovery being accidental. Mr. E. C. Acheson, whose patents are employed in this industry, was endeavouring to obtain crystals of carbon by melting together clay and carbon, the latter of which it was hoped might crystallize from the resulting reduced aluminum. Hard crystals were found after the fused mass had cooled, the component parts of which were concluded to be carbon and aluminum, and for which he invented the name "carborundum." Analysis, however, proved the new substance to contain silicon and carbon, and only a small quantity of alumina. Further experiments were made with mixtures of sand, carbon and salt as a fluxing agent, and large crystalline masses of carborundum were obtained. The substance thus formed corresponds to the formula CSi, is extremely hard, and is used in place of emery and corundum. In the manufacturing process the materials employed are sand, coke, salt, and sawdust; the coke is reduced to kernels of a certain size, to be used for making the "core," and other portions are ground to a fine powder for mixing with the charge of sand and salt. The original form of furnace was fitted with a pair of carbon terminals, which could be moved longitudinally, and was essentially an arc furnace, the chemical changes taking place being due to the high temperature of the arc passing between the carbon terminals. In 1895 this form was abandoned and a continuous electrical connection made between the terminals by the introduction of a "core" of granulated coke. By regulating the diameter of the core it could be heated to a sufficiently high temperature to convert the surrounding mixtures into carborundum. In the modern form of furnace the brick ends and carbon electrodes, with the necessary terminals for connecting up the current, are the only permanent portions. The charge, consisting of sand, finely-ground coke, and sawdust,—added to render the mixture more porous and consequently allow the gaseous products to pass through the mass—is placed in the furnace till it is on a level with the lower edge of the carbon electrodes. The coke "core " is then filled in, made into cylindrical form by hand, and finally surrounded at its sides and on the top by the remainder of the charge. Care is taken to prevent the mixture coming in contact with the carbon terminals, and necessary retaining walls are built up of bricks as the charging operation is proceeded with. The current is passed for thirty-six hours, and after cooling, the walls are taken down, unused "charge" raked off, and the outer crust of carborundum exposed. A cross section of the contents of the furnace presents many interesting characteristics. In the centre is the core, which has been, to a large extent, converted into amorphous carbon and graphite. From this there radiate beautifully coloured carborundum crystals to a distance of from ten to twelve inches. Next a thin inner crust of amorphous carborundum of a light green colour is met with, then the outer crust, also

amorphous, and beyond this, the unchanged mixture.[38] A curious effect is observed near the core, where the temperature is highest; here are found crystals of carborundum, from which the intense heat has volatilized the silicon, leaving "skeleton" crystals of graphite, while the silicon, passing outwards oxidizes to silica, and often presents the appearance of spun glass. Silicon itself has been found in the cracks in the bed of the furnace.[39] The carborundum is finally crushed, washed, and graded for the market.

Carborundum has a lower specific gravity than emery, and finds its principal application in the manufacture of wheels, stones, razor hones, rubbing bricks for marble dressing, paper, and cloth. The Canadian works of the Carborundum Company were destroyed by fire in 1903 and have not been re-built. This plant was comparatively small, only operating 200 horse-power. The factory, however, supplied the Canadian market, thus avoiding the payment of duty. The writer was informed by Mr. Acheson that most of the Canadian product was exported to Scotland, to be used there in finishing granite. The estimated cost of the crude crystals is 2.5 cents per pound, that of the treated powder, 4.5 cents per pound, while the selling price averages 9 cents per pound.

CORUNDUM.

The natural corundum industry of Ontario, which is of recent origin, is, however, now steadily growing in amount and value of output. The production of corundum in 1901 had a value of $53,115, and in 1903, $106,332, and in 1904 over $3,000,000.[40] The chief producing company, the Canada Corundum Company, has just completed a new mill of greatly enlarged capacity, and the other operating concern, which formerly exported the corundum-bearing rock to the United States, after cobbing it merely, is now crushing and treating it on the spot. Two additional companies are in process of organization for producing corundum.[41]

To the Canada Corundum Company, of which Mr. B. A. C. Craig is the president, may be accorded the credit of having placed the natural corundum industry of Ontario on a firm basis. Craig Mountain is said to be the largest deposit of corundum in the world. The hardness of this substance has long been known, and under the name of emery it has, in an impure state, been used as an abrasive agent. The product of this mine is said to contain from 95 per cent. to 98 per cent. crystalline alumina, and from letters the writer has seen, its hardness and cutting qualities seem

(38) Illustrated Catalogue No. III., Carborundum Company, N.Y.
(39) Electro-Chemical Industry, Vol. I., No. 2.
(40) Letter from Mr. B. A. C. Craig, President of the Canada Corundum Company.
(41) See 19 *bis*.

to have recommended it to consumers alike in Europe and on the American continent. Results are always the best tests of the efficiency of any agent, and the rapidly increasing market that Ontario's corundum is finding is sufficient evidence of the quality of this material. The Craig Mine is now putting out about ten tons a day, and the management confidently expect a considerable increase in the spring.[42]

GRAPHITE.

Though no company for the manufacture of graphite has yet been capitalized in Canada, the production of it by the Acheson process is carried on to a small extent in the Canadian branch of the Carborundum Company at Niagara Falls. The formation of the "skeleton" crystals referred to above suggested making use of the decomposition of carborundum for making graphite itself. The inventor's patents include the production of graphite in the form of pure electric-light carbon, by subjecting impure carbon to a high temperature for a sufficient length of time to volatilize the impurities;[43] the conversion of carbon into graphite by mixing with such metallic oxides as would be capable of forming metallic carbides, to be subsequently decomposed;[44] the conversion into graphite of such natural carbonaceous materials as contain uniformly intermixed through them metallic oxides sufficient to produce carbide, and thence graphite.[45] These processes throw considerable light on the scientific principles underlying the formation of this substance.[46]

X.—THE CEMENT AND PLASTER INDUSTRY.

The manufacture of Portland cement is mainly confined to Ontario, though one establishment—the Crescent Cement Works—is situated at Longue Pointe, in the Province of Quebec. In Ontario there are some fourteen companies and eight factories in operation, and throughout this Province are found the necessary raw materials (clay and marl) of an excellent quality. The development of the industry has been rapid, and has all taken place within the past few years. The most improved method of procedure is as follows: the marl is thoroughly mixed, mechanically, with water into a thin paste, and the same operation is performed with the clay. The two fluids are mixed thoroughly in the required proportions, and in a pasty condition are pumped into steel rotary calciners, about seventy feet in length and six feet in diameter, set at a slight angle to the

(42) See note 40. An account of the Corundum Industry of Ontario will be found in the "Canadian Mining Review," Vol. XXIII, No. 10, (1904).

(43) U.S. Pat. 542,982 of July 23, 1895.

(44) U.S. Pat. 568,323 of Sept. 29, 1896, and No. 617,979 of Jan. 17, 1899.

(45) U.S. Pat. 645,285 of March 13, 1900.

(46) Electro Chemical Industry, Vol. I., No. 2.

horizontal. These rotary calciners are the great feature of the Canadian cement plants. This form of kiln is originally of English origin, but has only been brought to its present effective condition since its introduction to this country. In the interior of the kiln are "channel-irons" running from end to end. At the lower end fuel is introduced in a particular manner, and the burning gases pass through the entire length of the kiln, and are allowed to escape at the upper extremity. At this latter end is introduced the "slurry" of the mixed ingredients, which becomes dried and finally calcined in the slow passage from one end to the other. The revolving irons carry the "slurry" up with them as they rise, and on reaching the top it falls, under the action of gravity, through the burning gases, being subjected at the hottest part to a temperature of 3,000° F., when combination takes place between the constituents of the fused mass, and the resulting "clinker" emerges into the vessel destined for its reception. The drying and calcining is thus performed in one operation, and no preliminary pressing of the material into bricks is required.[47] At the works of the National Portland Cement Company, recently erected at Durham, Ont., a great saving of time is effected by cooling the clinker in vessels drawn by an endless chain through a stream of water below the ground level. After cooling in this manner it is ground to a fine powder, and packed in bags or barrels ready for use. The whole operation by this process occupies only eight hours, a period of time which will be appreciated by all acquainted with the older methods. At Durham the raw materials are brought from the natural deposits, which are close at hand, calcined, cooled, ground and packed by means of a continuous series of mechanical conveyers from one part of the establishment to the other. This company has another plant in course of erection at Hull, P.Q., on the Ottawa River, which is intended to supply the Eastern Canadian market.

Several articles have appeared lately in the public press[48] pointing out that a possible over-production of cement may be the result of the numerous large concerns which are already in operation or are about to be started. Whether or not this will take place in the immediate future depends, naturally, on the general prosperity of the country and the consequent demand for building materials. Certainly cement has gained considerable reputation as a substitute for stone, as can be seen by the extent to which it is made use of by architects. It can be readily moulded into any form and may then be dressed to represent the natural article. If it can ever oust stone and brick from their present position depends, not only on its comparative cost, but on the quality of cement put out by manufacturers. One case of a collapse due to an admixture of a single bag of inferior material and the whole fabric of the cement industry

(47) The Portland Cement Industry: "Queen's Quarterly," Jan. 1903.
(48) "*The Globe*," Toronto, March, 1903, and other papers.

as supplying a substitute for the older building materials, will be in danger of a similar fate. The total output of Portland cement in 1902 was valued at 1,028,618 dols.,[49] and in 1903 at 1,166,497 dols.[50]

Gypsum is found in considerable quantities in Nova Scotia and New Brunswick. At Windsor, N.S., there are immense deposits; the beds found in the vicinity of Hillsborough, N.B., are, however, very large and of great purity, and form the basis of the most extensive operations.[51] It is also found in Ontario, and plaster works are located at Paris in that Province. In 1901 active operations were begun at Gypsumville, Manitoba. The industry, however is principally located in New Brunswick. Drawbacks in the way of freight charges, inadequate shipping facilities, and the competition offered by manufacturers of plaster of Paris in the United States, kept the industry from developing until the Intercolonial Railway was opened and the increased duty on American plaster imposed, when the New Brunswick plaster, quarried and prepared at Hillsborough, came to be firmly established on the Canadian Market. In manufacturing plaster of Paris, the stone is first dried in the air and ground—not burned in lumps as is still done to a considerable extent in England and on the Continent of Europe, and the pulverized material subjected to a process of calcination in kettles, of a capacity of sixty barrels of 300 pounds of the calcined plaster, furnished with lids and stirring arms which keep the material in constant motion. When the required temperature has been reached (285° F.), the plaster is removed and packed in paper-lined barrels for market. Analysis of the Hillsborough gypsum shows it to be 99.88 per cent. $CaSO_4$.[52] The principal markets for plaster of Paris are Canada, the United States, and South Africa, while the crude gypsum is exported largely to New York and other portions of the States, being used for making plaster for walls and ceilings.[53] According to the Geological Survey Reports for 1902, the gypsum produced in Canada during that year amounted to over 332,000 tons, valued at 356,317 dols.

XI.—CARBOHYDRATES: (A) THE REFINING OF SUGAR; (B) THE BEET-SUGAR INDUSTRY.

The hoped-for developments in the production of sugar from beets in Ontario and Southern Alberta, referred to in the first edition of this paper (1903) have not come up to the expectations either of the writer or of the public as will be seen from the sequel. Statistics show that during

(49) Geological Survey of Canada: Mineral Products, 1902.
(50) Stattisical Year Book, 1903.
(51) Geological Survey of Canada: The Mineral Resources of New Brunswick, 1899.
(52) Analysis by A. A. Breneman, of New York, in Mineral Resources of New Brunswick, Geological Survey of Canada, 1899.
(53) Letter from the Manager, Albert Manufacturing Co.

the last decade cane sugar has increased in production about 200 per cent. Judging from present appearances, and allowing for some slight tariff alterations, the increase in Canada should soon be in proportion to that of other countries.[54]

Raw sugar is imported from Cuba, the West Indies, Java, Manila, the Brazils, Mauritius, and the Continent of Europe. The most improved machinery and processes are employed, refined sugars and syrups being the staple products,

Belgium supplies to Canada the largest proportion of sugar, the imports from that country amounting in 1901 to 127,931,553 pounds; from Germany in the same year 83,941,290 pounds entered the country, the total imports being 336,694,833 pounds valued at close on $8,000,000.[55]

BEET SUGAR.

The most interesting point connected with the sugar industry is the way in which the production of sugar from beets cultivated on Canadian soil has become, in the past few years, an important factor in the country's progress. As far back as 1872 the Dominion Government sent a special agent to Europe to make a study of the industry. A bounty of $25,000 afterwards increased to $70,000 was offered by the Quebec Government in 1875 to the first successful factory to be established in a situation approved by the Government. This led to the establishment of a company known as the Union Sucriere du Canada, which, in 1881, erected the first of four proposed factories at Berthierville, Que.[56] This establishment was unsuccessful and only operated for a few days, mainly owing to the failure of the beet crop. After passing into other hands the plant was bought by an American company and removed to Eddy, New Mexico.[57] Another company was, in the same year, organized at Farnham, P.Q., not far from Montreal, which after some vicissitudes, did not deem its success sufficient to warrant a continuation of its operations, so sold its plant to a company at Rome, N.Y., in 1897. A third company, known as the Pioneer Beet Company started operations in 1881, at Coaticook, P.Q.,[59] and was successful in part, receiving a subsidy of 35,000 dols. from the Government, but it, too, closed its doors in 1883. The causes to which these failures may be attributed were lack of capital and enterprise, and the indisposition of the farmers to cultivate beets. The Agricultural Department of the Provincial Governments, however, continued experimenting with various kinds of beets and studied the conditions most favour-

(54) Letter from Mr. D. A. Gordon, President of the Wallaceburg Sugar Company.
(55) Essay, Mr. Read, University of Toronto.
(56) Report of Dominion Government on beet sugar manufacture in Canada.
(57) Letter from the Manager of the Dresden Sugar Co., Ontario, now removed to Michigan.

able to their successful growth. For some years past the Ontario Agricultural College at Guelph has, as a consequence of the excellent results obtained at their experimental stations, been carrying on an educational campaign among the farmers of the Province. As a result of this the quality and tonnage of beets now grown in different parts of Ontario surpass those of many American States. The climate of this Province, with its sunshine and long autumns, is peculiarly favorable to the cultivation of the beet, which takes about four months and a half to reach maturity. It requires, however, to be demonstrated to the farmers that the cultivation of beets will pay them better than other land produce before the requisite supply of suitable material will be obtained. That the profits are large can be gathered from the fact that wheat yields in Ontario $15 an acre per annum, oats, $9.74, and beets for sugar, $60. In the last case the cost of production is necessarily large, owing to a great amount of labour being required, but, all the same the profits to the farmer should, with skilful treatment, be at least $30 per acre per annum. The beet tops are of value as a fertilizing agent owing to the salts they contain, and find a use also as a food for cattle. In 1901 beets were grown —under instructions from the Agricultural Department—in fifteen districts of Ontario, and the average yield per acre was over seventeen tons of a high quality of beets which gave an average of 15.6 per cent. of sugar of an average purity of 87.7 per cent. All this points to a future for Ontario as a sugar-producing country; this fact has been fully realized by the Provincial Government, which offered a bounty of $275,000 for three years,[58] and at its recent session extended this bounty for a further period of two years, to be distributed among factories according to the amount produced. Four companies were organized a few years ago, namely, the Wiarton Beet Sugar Company (capital $500,000) which has since been shut down; the Dresden Sugar Company (capital $600,000) which has now removed its factory to Michigan; the Wallaceburg Sugar Company (capital $500,000) and the Ontario Sugar Company, of Berlin (capital $1,000,000); each of these companies received a bonus from the town where it was situated, averaging $28,000. The capitalization of a company engaged in this industry depends entirely on the size of the plant, a general estimate of $1,000 per ton of beets per day may be considered a fair calculation of what would be required.

Two companies only are thus in the field this year, and it seems reasonable to expect that both factories will increase their output over that of 1903. The nearness, geographically speaking, of the Wallaceburg and Dresden concerns to one another—some nine miles apart only—militated against their success, and it is to be hoped that now the former is, so to speak, alone, it will do better than heretofore.

(58) 1, Edw. VII., Cap. II, (1901).

Beet sugar factories have also been established in Alberta, in the North-West Territories of Canada. Since 1893, an area of about 300,000 acres has been made productive by means of the irrigation system of the Canadian North-West Irrigation Company, and a portion of this area has been utilized for beet cultivation, principally by the Mormon settlers. The most important factory has been established by the Knight Sugar Company at Raymond, south of Lethbridge, on the Canadian Pacific Railway. The capital of this company is $1,000,000. The area intended to be planted with beets is 3,000 acres, and the daily capacity of the factory will be 400 tons of beets per day. The only difficulty which the industry is encountering in the North-West is the scarcity of labour.[59] This is due partly to the scanty settlement of the country, and partly to the superior attractions of the mining regions, which are situated at no great distance.

A plentiful water supply, lime, and source of power, are necessary for the profitable prosecution of the industry; all this has been carefully considered in locating the factories enumerated above, steam power being employed for pumping and the working of all machinery. There is room for many more factories in the Dominion; according to Dr. A. B. Shuttleworth, Chief Agriculturalist to the Ontario Sugar Company, whose name is indissolubly connected with the development of beet cultivation, it would require over thirty refineries each of 600 tons capacity to supply the home market alone.[60]

The working season of a factory runs for about 100 days, operating continuously. The cost of the sugar is from three to three and a half cents per pound, and the profits to the makers are estimated at fifty cents per ton of beets used. This would mean that in a factory of 500 tons capacity, working for 100 days, the profits would amount to $25,000.

The scope of this article does not allow of any detailed consideration of the working process by which the sugar is extracted frm the sliced beets and crystalized. New proceses are being employed for utilizing the residual molasses. This is treated for the recovery of the sugar in some part, and also for the production of alcohol by fermentation. An American company in 1901 produced 915,000 gallons of alcohol in this way, of a quality considered to be quite equal to the grain product. Another new process is that of the manufacture of syrup from the beet instead of sugar; forty gallons of this can be obtained from a ton of beets, which, at thirty cents a gallon, means a return of $12 per ton of material used, while the product in sugar yields only from $7 to $8 per ton of beets. The

(59) Letter from Manager of works at Raymond.
(60) Berlin News Record, Nov. 8, 1902.

beet-pulp refuse is also being largely used as a food for live stock, for which purpose it is extremely suitable owing to its nitrogen contents. In this connection a new process has been introduced for drying the pulp, which entails an expenditure of $5 per ton, but, as the dried pulp is sold at $6.25 per ton, a clear profit of $1.25 is thus secured to the manufacturer.[61]

The production of sugar from Canadian grown beets is a new and, it is to be hoped, rising industry which offers great scope for some co-operative arrangements between the companies and the farmers. It should give an impetus to agriculture, afford employment to thousands of unskilled workpeople, and, as an important industry, be a lasting benefit to the country. Whether or not the growing of beets will become popular remains to be seen; the present quality is as yet not so good as was expected, but much may yet be done in the way of improvement by careful cultivation.

The following communication, dated March 6th, 1903, from Mr. George Elsey, manager of the Dresden Sugar Company, conveys some idea of the position of the industry from the point of view of the manufacturer and its possible future:

"At the present time there were four factories which operated this last season, and from what we are able to learn the results were as satisfactory as could be expected under the existing conditions, that is, the rain fall last summer damaged the beet crop from fifty to sixty per cent., both in the United States and in Canada. The balance of the crop, on account of wet weather, cost considerably more to raise than what was necessary. It was unfortunate that this should occur in the first season that the factories were started in Canada, as it was very disappointing, but most of the farmers have told us that they were surprised at the amount of rain the beet would stand, and in several instances where they could harvest the beet crop, the corn and other crops were ruined. After we have had a seasonable year and it will be demonstrated to the farmers that there is more money in raising sugar beets than any other crop that grows, the four factories now in existence will get their supply of beets within hauling distance of the factories. . . . Our farmers know well that the Michigan farmers obtain about a dollar a ton more for their beets than they do, and they also understand that it has cost as much in money and labour to raise a ton of beets in Canada as it does in Michigan or any part of the United States. They therefore feel dissatisfied, and are clamouring for more money, which the companies would be glad to pay if they could sell their sugar for the same price as the American Beet Sugar refineries. The present Canadian sugar tariff is such that it would not allow any

(61) In the above I have drawn largely from an essay on the beet-sugar industry by Mr. E. R. Read, a student in the Department of Political Science, University of Toronto, who kindly placed his papers at my disposal. Also from Dr. Shuttleworth's article in the "*Berlin News Record*," 1902.

more sugar refineries to be built in Canada. The companies that are already here have the experience of what this tariff can do. It allows sugar that has been refined in the United States to be shipped in here and undersell Canadian refined sugar, which means a loss to the refineries and to the Canadian people. It allows raw beet sugar to be imported at a price that will prevent the farmers from taking hold of the beet industry as they should. Canada is sending to Germany and other foreign countries about $1,000,000 per month for raw beet sugar, and the naturally yearly increase of consumption is about eight per cent, so that the future of the sugar beet industry, under a proper tariff, would be a lasting one and a great benefit to the farming community."

XII.—NATURAL GAS AND PETROLEUM.

NATURAL GAS.

The existence of natural gas in Ontario was first discovered in 1889, being found in two well-defined areas, as the Essex county field and the Welland county field. It is chiefly near Buffalo, on Lake Erie, and near Windsor, Ontario, that the largest supplies are met with, though practically it may be got in nearly any part of the Niagara peninsula in small quantities. In 1901 there were 158 wells in operation, and 368 miles of piping were needed to distribute the gas. Much of the gas produced in Essex county was formerly led across the river to Detroit by pipe lines, but on representations made by the people of the Essex district to the effect that the supply of gas was not sufficient for home consumption, the Ontario Government passed an Order in Council in October, 1901, prohibiting the gas from the Essex field being exported to the States. None of the product of this natural gas field is therefore now being sent across the Detroit river; it is, however, still exported from the Welland field to the American side of the Niagara River, chiefly to Buffalo, N.Y. It may be mentioned that the landowners on whose farms the wells are located get their gas free in addition to being paid for the use of their lands.[62] The value of the gas produced in Ontario during the last ten years shows considerable fluctuations, being much less in 1903 than in the previous year, due, no doubt, to the Government prohibiting its export.[63]

PETROLEUM.

This is one of the chief mineral products of the Dominion, though as yet the output is not sufficient to meet Canada's needs. The principal seat of the industry is at present in Ontario, where commercial quantities

(62) Report of the Bureau of Mines, Ontario, 1902.
(63) Statistical Year Book of Canada, 1903.

are found in the counties of Kent and Lambton. In the former there are two oil fields, one at Oil Springs, extending over 1,200 acres, and the other in the Petrolea district, 20 miles long by 2 wide.[64] In Lambton county the industry dates back to the year 1862. Petroleum is also found in Quebec, Nova Scotia, New Brunswick, and boring operations that have in recent years been carried on at Athabasca, near Edmonton, in the North-West Territories, point to a likelihood of that part of the country contributing largely to the future supply of mineral oil.

The industry is now one of the most highly organized in the Dominion; the system of drilling and pumping now used—the "jerker-line" system enables a well yielding from eight to ten gallons a day to be profitably worked. This system has gained for itself a world-wide reputation; it is used in Galicia, Russia, Afghanistan, Burmah, India, Italy, France, California, and Australia. Its advantages are numerous; a central engine can operate a large number of wells; on one property near Petrolea, 233 wells, scattered over an area of 400 acres, are worked by a single engine. It is estimated that to sink a well of about 500 feet in depth costs only $125.[65] In 1900, there were approximately 10,000 wells in operation, yielding on an average seventy-one barrels of oil each.

The refining side of the petroleum industry is largely in the hands of the Imperial Oil Company,[66] which some years ago absorbed several other concerns, and of the Canadian Oil Refining Company. The plant of the former at Sarnia has a capacity of 60,000 barrels of crude oil per month, and the market for their products reaches from Halifax to Vancouver. Many of the bye-products of the refining process find a market in England and in Spain. The latter company have erected an up-to date plant at Petrolea, on the site of one which was in operation some years ago, where all the products will be manufactured that modern science shows can be obtained from petroleum.[67] Improvements in methods of retort ng have recently led to considerable quantity of the crude oil being used for gas making, three and a half million gallons being an estimate of the amount so employed.[67]

There has been a slight falling off in the production of oil during the past years; calculated as "crude" oil, the output in 1901 was 27 millions Imperial gallons, and in 1901 a little over 26½ millions.[68] In 1903 it fell to some 16 million gallons. A slow process of diminution seems to be going on in the area at present productive, and a falling off must be looked for

(64) The oil is found at depths varying from 370 to 400 feet.

(65) This and much of what is given here on natural gas and petroleum is from a paper by Mr. W. J. K. Vanston, read before the Canadian Section of the Society of Chemical Industry in Jan. 1903.

(66) Capital stock, $1,000,000.

(67) Bureau of Mines Report, Ontario, 1902.

(68) Statistical Year Book, 1903.

from year to year unless this is counteracted by an extension of the oil-bearing territories.[67] Probably, the field about to be exploited in the North-West will alter the position somewhat, and an increase in the output may be confidently looked for.[69]

XIII.—PULP AND PAPER.

PULP.

As timber is one of the chief natural products of the Dominion, it is only to be expected that Canada should figure largely in the wood pulp industry; the figures that might be given to indicate the number of cords of pulp-wood available throughout the country are so large that one could hardly grasp their real significance. The industry is not so young as many others that have been considered; in the census of 1871, no pulp-making plants are mentioned; in 1881, there appear five mills, employing 68 men, and having an output valued at $63,000; in 1891 there were 24, with a yield valued at more than a million dollars; while 1903 shows some 39 factories, from which the exported pulp alone amounted to over five million dollars.[70] The area of pulp-making operations is not confined to any one Province, New Brunswick, Nova Scotia, Quebec, Ontario, and British Columbia are all represented in the industry.

The principal woods employed for pulp-making are white and black spruce, balsam, poplar, and pine; spruce[71] and balsam are those most generally used, on account of the special quality of their fibre and their colour, pine being utilized mostly for chemical pulp. The two main varieties of the pulp are *mechanical* and *chemical*. The former is obtained by grinding spruce logs to powder, the logs being pressed against a rapidly revolving grindstone, with water constantly supplied to prevent the friction causing a rise in temperature. A liquid pulp is thus obtained from which the water is squeezed by hydraulic machinery, a pressure of many tons to the square inch being employed. The resulting pulp still contains water, however, to the extent of from 50 to 60 per cent., though some works—notably those at Sault Ste. Marie—have introduced a machine specially constructed for the purpose of removing this large excess of moisture. Where the pulp is to be made at once into paper, this drying process is unnecessary. The specially dried pulp resembles paper very closely in outward appearance.[72] Chemical pulp is prepared by disintegrating and

(69) Total value of products of petroleum in Ontario in 1901, $1,467,940, Bureau of Mines Report 1902.

(70) Statistical Year Book, 1903.

(71) In 1894 it was estimated that Canada contained between 38 and 40 per cent. of woodlands and forests, or about 1,400,000 square miles, one-half of this being spruce. The spruce area is thus 450 million acres. In all there are 4,500 million tons of pulpwood in sight. "Pulpwood of Canada." Pan-American Exhibition pamphlet, published by the Geological Survey, 1901.

(72) The Sault Ste. Marie Works used (1903) some 200 tons of spruce logs yielding 150 tons of pulp per day.

extracting the resinous matter from the wood —in the form of chips— by digestion with sulphur compounds, usually a weak solution of sulphurous acid, about a quarter of which is in the form of bisulphite of lime.[73] A soda chemical process is also employed by some makers. The sulphur used for the production of sulphurous acid is either imported from Sicily or obtained by burning pyrites. Chemical pulp possesses many advantages over mechanical pulp, though its manufacture is necessarily more expensive, and the yield per cord of wood, as compared with the latter, is much less.[74] It has a longer and tougher fibre, and the resinous matter being no longer contained in it, finds uses for qualities of paper for which the mechanical pulp would be unsuitable. The principal markets for pulp are Great Britain, the United States, France, Australia, and Japan. Much of it is used, however, locally for the manufacture of paper. In 1903 the requirements of Great Britain alone amounted to $12,000,000, a little over seven per cent. of her needs.

PAPER.

In many cases the producers of pulp also manufacture it into paper. The principal requisites for the paper industry are a plentiful supply of pulp-wood, good water and an abundance of it, and cheap power; all these can be found in many parts of Canada. The growth in the demand for paper of all kinds, news, wrapping, wall and the finer grades, was one of the features of last century—especially newspaper. The introduction of wood fibre into its manufacture has consequently enabled the supply to keep pace with the demand. The process of manufacture requires no description here; the secretary to a prominent Canadian firm states that originally they used rope as a raw material, then straw, which was abandoned for rags, and finally these gave place to chemical and ground wood-pulp. Previous to 1870 no wood whatever was used in the manufacture of paper in this country. Ground wood-pulp was introduced at that time and has since become the filling material of the cheaper grades of paper, being partly pasty and partly fibrous. Up to 1885 the real fibre—the framework of the paper —was supplied by rags. In 1885 sulphite pulp was introduced and has largely replaced rags, except in the higher grades of paper, in which linen is used, and in the very low grades, where straw is employed.[75]

The *Toronto Globe* of March 4th, 1903, in an article on the wood-pulp industry, gives the following statistics, which are of interest:—

	Tons.
Production of mechanical pulp in 1902	152,210
Production of sulphite pulp in 1902	76,735
Production of soda pulp in 1902	9,044

(73) Letter from Mr. Carl Riordan, Merritton, Ont.

(74) One ton of mechanical pulp requires a little over a cord of wood; one ton of chemical pulp requires a little over two cords of wood.

(75) Mines Report, P.Q., 1901.

XIV.—ASBESTOS AND MICA.

ASBESTOS.

This mineral occurs in large deposits in the "Eastern Townships" of Quebec, where it was first worked in 1878; from 1880 up to the present date the production of asbestos has increased steadily; the output that year is given as 380 tons, while in 1901 over 38,000 tons are recorded in the returns furnished by the producers. The world's supply of asbestos is, for the most part, obtained from Canada, and the Quebec deposits have in the past proved to be the most profitable mineral mined in the province. Thirteen mining companies are at work in this industry, which is principally carried on at Thetford, Lac Noir, and Danville, giving employment to approximately 1,000 men. Asbestos is shipped largely to Great Britain, the United States, Belgium, Germany and France.

MICA.

Another silicate found in Canada is mica, which, though occurring in small quantities, is a not unimportant industry; in Ontario there are several mines and a number of works where splitting, trimming, and sorting the material into saleable sizes is carried on. The Provinces of Ontario and Quebec produce the greater part of the mica used in the manufacture of electrical apparatus in the United States, and also export not inconsiderable quantities to Great Britain. The so-called "amber" mica, or phlogopite, is preferred for this use to other varieties on account of its superior flexibility and the thinness of the sheets into which it can be split. The mica mines of the General Electric Company in Ontario produce large quantities of mica annually, and the Company have trimming works at Sydenham and Perth. There are also important mica trimming plants in Kingston and Ottawa.[76]

CONCLUSION.

The new Canadian Niagara Power Company, whose works are in the course of construction at Niagara Falls should give a fresh impetus to the development of industrial chemistry locally. This will be the first company to produce power on the Canadian side of the Falls. A feature in the plant is the size of the generating units, each of which will have a capacity of 10,000 horse-power. They will be more economical than generators of 5,000 horse-hower, will occupy but little more space and their cost will be much less per horse-power in comparison. It is expected that the output of the company will be used principally for Canadian industries and for such public utilities in the Province of Ontario as may be within reach of long-

(76) Letter from Mr. Thos. W. Gibson, Director of Bureau of Mines, Ontario.

distance transmission. The power on the American side is employed by some twenty or thirty firms engaged in such chemical industries as the manufacture of pulp and paper, silver plated goods, chlorate of potash, caustic alkali, salts of tin, carborundum, carbide, graphite, pure metallic lead, "alundum"—another emery substitute,—cereal food-stuffs, nitric acid and composite boards made from wood-pulp and flax-fibre. Judging from all this there should be a large increase in the number of chemical industries in this neighbourhood when the Canadian power station is completed and the current available from the Falls to Toronto.

The subjects that have been considered in this paper do not by any means exhaust the catalogue of chemical industries in Canada. Many important manufactures have, for the reasons mentioned in the opening paragraph, been omitted. A short summary of these will suffice. Matches, for example, constitute an important and necessary article of daily use, and are made in enormous quantities, practically all that are used in Canada being manufactured in the country. Brewing and distilling are carried on extensively also, ale, lager beer, and stout being made, while Canadian rye whisky is known throughout the whole English speaking world; even a "Canadian Scotch" is produced at Perth, Ont.; brandy and champagne and other wines are made at Hamilton, Brantford, and Pelee Island, on Lake Erie. Fruit canning is one of the great industries of Wentworth and Essex Counties, Ont.; bacon packing and salmon canning may also be classed among those manufactures requiring the careful supervision of the skilled chemist. To the list may be added explosives of all kinds; blackings, varnishes, japans, lacquers, paints and shellac, foodstuffs and sauces; antitoxines for use in the practice of medicine are made by the Parke Davis Co. at Walkerville. Natural mineral waters are abundant, at St. Catherines, in British Columbia and in Quebec, while manufactured aerated waters are made in mostly all the important towns. The almost universal wearing of india rubber foot coverings during the winter season necessitates the production of large quantities of goods of this sort. Many large factories for this purpose are in existence from which rubber goods of a superior quality emanate; dyeing and calico-printing might also be mentioned as being in a flourishing condition. The attitude of manufacturers towards chemists has of late years been extremely favourable, and many have seen it to be to their advantage to employ men trained in our universities to investigate the processes and materials employed in their particular industries. So far their employment has been amply justified by the results, and it is to be hoped that more may be brought to see the profit to be gained by adopting scientific methods of work. The university man who has specialized in chemistry can assist the manufacturers in this by bringing to bear on the *rationale* of the technical processes the general scientific knowledge which he

has gained during his college course, and his experience of methods of research and manipulation; he can thus materially benefit his employer by improving the quality of his products or enabling him to turn out his goods at a cheaper rate. Let the manufacturer, be he dyer, tanner, pulp-maker, or ironmaster, indicate only that he is willing to find employment for men educated in the higher branches of scientific work, and the universities of the Dominion will supply them. Where chemical processes are used, it is essential for the prosperity of this country that all the available scientific knowledge should be brought to bear on them, in order that they may continue to improve and to develop even more than they have done in the past decade. Canada, with its immense natural resources, and its water power should, in time and with proper management and assistance in the lines indicated, become one of the largest producers of the world's supplies.

In conclusion, I wish to acknowledge the great assistance I received in preparing the previous edition of this paper, from Mr. Fred P. Clappison, B.A., then Fellow in Political Science in the University of Toronto, who gathered together for me from all quarters much of the information required for this short and imperfect account of the chemical industries of the Dominion. In particular his help in connection with the statistics contained in the text and in the appendices was invaluable. Much of what appeared before has been repeated, though many alterations, omissions and additions have been necessary. To the gentlemen who so kindly answered enquiries as to their particular industries and placed valuable material at my disposal I desire also to convey my hearty thanks.

APPENDIX I.

THE IRON ORES OF CANADA.

Nova Scotia.—Magnetites in enormous quantities at Nictaux, in Annapolis County, at Whyhogomah, in Inverness County. Specular and red hæmatite at Nictaux, Stewiacke, Pictou, Antigonish, Guysboro, East Bay, and many other points. Limonite, specular, spathic clay ironstone and hæmatite at Londonderry. Mineral fuel and fluxes are in close proximity throughout the whole district.[77]

Cape Breton.—Extensive deposits of brown hæmatite, magnetite, and spathic ores lying adjacent to the great coal-fields.[78]

New Brunswick.—Magnetite and bog ores. Coalfields at Grand Lake and hardwood throughout the Province.

Province of Quebec.—Very extensive deposits of bog and lake ores, extending from the Province of Ontario to Gaspe, Magnetite deposits especially good at Sherbrooke, Leeds, Sutton, St. Jerome, and in Pontiac County. Hardwood and limestone abundant. Deposits of chrome-ironstone found in 1895 in Coleraine. The "Eastern Townships" obtain iron by dredging in the Lac-a-la-Tortue. Magnetites at Hull, near Ottawa.[79]

Ontario.—Vast deposits from the Ottawa Valley to head of Lake Superior, comprising magnetite, red hæmatite, limonite, specular, and occasional bog ores. The Helen Mine, at Michipicoten, is said to be one of the richest in the world. There are also extensive forests of hardwood, especially suited for the production of charcoal, and fluxes in abundance.[80]

Manitoba.—Magnetite, hæmatite, and bog ore on Lake Winnipeg. Hardwood in adundance.[81]

British Columbia.—Magnetic ores at Texada Island and Cherry Tree Bluff. Coal and wood in plenty. Collieries at Nanaimo (Naval coaling station for H. M.'s ships), Wellington, and Comox. A recent discovery of large deposits of magnetite has been reported in the Boundary Region, which at present mainly finds a use as a flux.[82]

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(77) Nova Scotia Report of Mines, 1901.
(78) Report of Geological Survey.
(79) Mines and Minerals of Quebec, Dept. of Mines.
(80) Bureau of Mines Report, Ontario, 1901.
(81) Geological Survey of Canada, 11th Annual Report.
(82) Geological Survey of Canada, 11th Annual Report

APPENDIX II.—METALLIC PRODUCTION OF CANADA, 1892-1903.

Metals.	Value, 1892.	Value, 1897.	Value, 1901.	Value, 1902.	Value, 1903. ‡
Pig Iron.....	637,421 dols	53,796 tons.	1,212,113 dols. †	1,043,007 dols.	707,838 dols.
Copper in Mattes.....	818,580 " *	1,501,660 dols. *	6,096,581 " †	4,511,383 "	5,728,261 "
Nickel in Mattes.	1,399,176 " *	1,399,179 "	4,594,523 " *	5,025,903 "	5,002,204 "
Arsenic.	1,000 "	.....	41,676 " †	48,000 "	15,420 "
Gold.....	907,601 "	6,190,000 "	24,128,503 " †	21,336,667 "	18,834,490 "
Silver	193,441 "	2,613,173 "	3,265,354 " †	2,238,351 "	1,170,779 "
Aluminum.....	.....	.....	1,000,000 "	1,643,250 "	.....
Lead.....	49,422 "	1,396,853 "	2,249,387 " †	934,095 "	762,660 "

* Value of metal if refined. † Statistical Year Book, 1903.

‡ Subject to revision, Mr. T. W. Gibson states that the total pig iron and steel produced in Ontario in 1903 amounted to 87,004 tons and 15,229 tons respectively; the whole of Canada yielded, during the same period, 265,418 tons of pig iron and 232,641 tons of steel.

APPENDIX III.‡—IRON AND STEEL PRODUCTION.

Company.	Plant at	Built.	Source of ore.	Employees, 1902.	Output in Tons.				Capacity of Furnaces in tons per day.		Capitalization.
					Pig Iron.			Steel.			
					1892.	1901.	1902.	1901.	1892.	1902.	
											Dols.
Canada Iron Furnace Co...	Midland, Ont....	1899	Ontario.....	..	..	18,948	..	..	..	..	1,000,000
	Radnor, Que.....	..	Quebec.....	..	5,574	31,159	..	..	40	..	..
	Londonderry, N.S.	1887	N.S.....	*	28,052	*	*	*	40,000 per ann.	150	..
Hamilton Steel & Iron Co.....	Hamilton, Ont....	1896	Ontario and U.S.A.....	1,000	† 1,000	..	51,701	9,473	†	..	1,500,000
Nova Scotia Steel and Iron Co....	New Glasgow, N.S.....	..	N.S..	965	29,502	28,407	..	23,916	100	100 pig,	5,000,000
Deseronto IronCo.	Deseronto, Ont ..	..	U.S.A.....	..	..	13,701	..	..	..	100 steel	..
Dominion Steel & Coal Co.....	Sydney, N.S.....	1901	Newfoundland.	6,000	†	27,643	191,259	86,424 (1902)	†	1,000 pig, 800 steel	33,000,000
John MacDougall and Co.....	Drummondville, Que.....	..	Quebec	..	..	793	..	..	6	..	..
Cramp Ontario Steel Co.....	Collingwood, Ont.	1900	Ontario and foreign....	†	..	..	..	..	..	200,000 per ann.	..
Lake Superior Power Co.....	Sault Ste. Marie.	1901	Ontario.....	500	..	..	..	..	†	..	117,000,000

* Not in operation, due to repairs being made. † Not in operation. ‡ Prepared by Mr. F. P. Clappison in 1903, largely from private letters.

APPENDIX IV.*—PORTLAND CEMENT AND PLASTER OF PARIS.

Firm or Company.	Place.	Capital.	Capacity of Plant in barrels per annum.	Output, 1902	Date of Beginning Manufacturing.
		Dols.			
Canadian Cement Co.....	Longue Pointe, Que....	200,000	....	....	....
Canadian Portland Cement Co.	Deseronto, Ont.....	1,500,000	250,000	250,000	1893
Lakefield "	Lakefield, Ont.....	590,000	75,000	75,000	1902
Imperial "	Owen Sound, Ont....	250,000	50,000	50,000	1902
Grey and Bruce "	" "	100,000	30,000	20,000	1902
Owen Sound "	Shallow Lake, Ont....	199,000	100,000	100,000	....
Sun "	Owen Sound, Ont....	500,000	40,000	40,000	1902
National "	Durham, Ont.	1,000,000	300,000	....	1903
Hanover "	Hanover, Ont.....	150,000	30,000	30,000	....
		4,399,000			
Albert Manufacturing Co., (Plaster of Paris).....	Hillsboro', N.B.....	350,000	....	60,000	....

* See Note ‡ in Appendix III.

APPENDIX V.—SUGAR FROM BEET ROOTS.

Company.	Place.	Capital.	Began.	Out put.* July 02—July 03	Out put.* July 03—July 04.	Capacity in tons of beets per day.
		Dols.				
†Wiarton Beet Sugar Co.....	Wiarton, Ont. ...	500,000	1901	1,565,000 lbs.	981,000 lbs.	350
Ontario Sugar Co.....	Berlin, Ont.....	1,000,000	"	6,063,926 "	7,059,695 "	600
‡Dresden Sugar Co.....	Dresden, Ont.....	600,000	"	3,763,987 "	2,094,999 "	600
Wallaceburg Sugar Co.....	Wallaceburg, Ont.	500,000	"	3,606,604 "	4,230,422 "	700
Knight Sugar Co.....	Raymond, N.W.T.	1,000,000	"	.....	.....	300

* Letter from Mr. C. C. James, Deputy Minister of Agriculture, Ontario. † Now closed down. ‡ Removed to Michigan.

14

The Action of Nitrate of Silver on Di-sodium Orthophosphate in Dilute Solution.

By William Robert Lang and William Perot Kaufmann.

[Reprinted from The Journal of The American Chemical Society, Vol. XXVII. No. 12. December, 1905.]

THE ACTION OF NITRATE OF SILVER ON DISODIUM ORTHOPHOSPHATE IN DILUTE SOLUTION.

By William Robert Lang and William Perot Kaufmann.

Received July 14, 1905.

The generally accepted text-book expression for the reaction which takes place between solutions of disodium orthophosphate and nitrate of silver is given as being

(1) $\underbrace{Na_2HPO_4}_{142.1} + \underbrace{3AgNO_3}_{509} = Ag_3PO_4 + 2NaNO_3 + HNO_3,$

indicating the complete precipitation of phosphoric acid as a silver salt and the setting free of nitric acid.

From the molecular weight in (1) it will be seen that 1 gram of disodium orthophosphate should react with 3.57 grams of silver nitrate.

In order to determine the correctness of this expression, decinormal solutions of these were made up and the phosphate titrated with the silver nitrate, using potassium chromate as an outside indicator. As the result of from 200 to 300 determinations it was found that the "end-point" of the reaction, as indicated by the first appearance of the red silver chromate, invariably occurred when an amount of silver solution had been added corresponding to the proportion of 1 gram of disodium orthophosphate to only 1.447 grams of silver nitrate. These proportions would indicate that a reaction had taken place as expressed by the equation

(2) $2Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + NaH_2PO_4 + 2NaNO_3.$

Ostwald, in his "Scientific Foundations of Analytical Chemistry" (second English edition, 1900), on page 204, gives this equation (2) as being probably the more correct expression of the reaction taking place between these substances, but adds that, ". . . . . it no doubt also fails to express all that goes on."

The analyses of types of the resulting silver phosphates may be tabulated as follows:

The figures in column (*e*) comparing the even with the odd, show that a greater yield of precipitate is obtained from the neutralized solutions than from those reacting acid, and a comparison of the yield of precipitate *obtained* and *calculated* in the case of the

TABLE I.

a. Reaction of solution.	Grams Na_2HPO_4 used. *b.*	Grams $AgNO_3$ used when "end-point" with K_2CrO_4 was reached. *c.*	"End-point" overstepped. *d.*	Grams precipitate yielded. *e.*	Calculated yield of precipitated Ag_3PO_4 from grams $AgNO_3$ in columns *c* and *d*. *f.*	Calculated yield from grams Na_2HPO_4 in column *b*. *g.*	Grams Na_2HPO_4 not acted on by $AgNO_3$. *h.*	Percentage of silver in precipitated phosphates. *j.*
(1) Acid	0.7105	1.17872	.....	0.9608	0.9700	2.09	0.4 (=57%)	76.96
(2) Neutralized by dilute KHO	0.7105	1.17872	.....	0.9655	0.9700	2.09	0.4 (=57%)	75.82
(3) Acid	0.7105	.....	1.696 (excess)	1.0630	1.734	.....	.....	76.19
(4) Neutralized by dilute KHO	0.7105	.....	1.696 (excess)	1.4070	1.734	.....	.....	76.80
(5) Acid	0.7105	.....	2.544 (large excess)	1.1350	2.601	.....	.....	76.65
(6) Neutralized as No. 4	0.7105	.....	2.544 (large excess)	2.3841	2.601	.....	.....	77.36

neutralized solution makes it evident that even in such menstrua the phosphate enters appreciably into solution.

It will be seen from (1) and (2), which are typical of a large number of determinations, that the "end-point" occurs at a stage in the reaction where only a partial separation of the phosporic acid as the silver salt has taken place. The resulting solution is acid to litmus, which acidity is due to the dihydrogen sodium orthophosphate; no free nitric acid could in any case be detected at this stage. It is evident, however, from these determinations and from Nos. 3, 4, 5 and 6 that equation (2) only expresses accurately what takes place when silver nitrate is added to disodium orthophosphate and the completion of the reaction taken as being indicated by the first formation of argentic chromate.

As from these results it was evident that there remained a considerable quantity of phosphoric acid in combination as (presumably) dihydrogen sodium orthophosphate, silver nitrate was added in excess to effect its complete precipitation, if possible, and the precipitates analyzed. The results are expressed in percentages of silver which was determined first of all gravimetrically, but later on Volhard's method was substituted on account of the close agreement of the gravimetric estimations. The only one of the percentages in column (*j*) which *accurately* corresponds to the substance Ag_3PO_4 is No. 6, the others showing a deficiency in their silver content of from 0.4 to 1.54 per cent. But in the earlier stages of this investigation in four cases precipitates were obtained which yielded, on analysis, respectively:

	Silver. Per cent.
(1) "End-point" reaction	73.76
(2) "End-point overstepped	74.19
(3) Large excess of silver nitrate	73.88
(4) Deficiency of silver nitrate	73.62
Average	73.862

These precipitates evidently correspond exactly to the formula $Ag_5H(PO_4)_2$ which contains 73.86 per cent. of silver. The others in Table I, numbered (1) to (5), lie between somewhere Ag_3PO_4 with 77.32 per cent. and $Ag_5H(PO_4)_2$ with 73.86 per cent. of silver.

The following table contains the percentage of silver found in a number of precipitates obtained under similar conditions of temperature and concentration, but in different total quantities

of the reacting salts. We have found it so far impossible to produce at will the phosphate of any desired composition but hope that further investigation will enable us to accomplish this.

TABLE II.—SILVER CONTENT IN PERCENTAGES.

73 per cent. and below 74 per cent.	75 per cent. and below 76 per cent.	76 per cent. and below 77 per cent.	77 per cent. and above.
73.49	75.34	76.47	77.01
	75.23	76.17	
	75.95	76.77	
	75.01	76.47	
	75.78	76.25	
		76.70	
		76.43	
		76.52	
		76.35	
		76.82	
		76.57	
		76.96	
		76.25	
		76.23	

It will be seen from this that the most commonly occurring precipitates nearly approach that of the composition Ag_3PO_4 *but not quite.*

Having obtained the "end-point" with potassium chromate (the reaction expressed by

$$2Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + NaH_2PO_4 + 2NaNO_3),$$

and having filtered off the precipitate, an excess of silver nitrate was added, causing further precipitation of a phosphate containing 76.25 per cent. to 76.5 per cent. of silver. The filtrate from this further precipitate was found to contain free nitric acid and also responded to tests for phosphoric acid. Following the equation given above, it would seem that the dihydrogen sodium phosphate reacted further with the silver nitrate possibly in accordance with the following equations:

(3) $$NaH_2PO_4 + AgNO_3 = AgH_2PO_4 + NaNO_3,$$

(4) $$AgH_2PO_4 + AgNO_3 = Ag_2HPO_4 + HNO_3,$$

(5) $$Ag_2HPO_4 + AgNO_3 = Ag_3PO_4 + HNO_3.$$

Combining these equations there would be obtained the expression

(6) $$NaH_2PO_4 + 3AgNO_3 = Ag_3PO_4 + NaNO_3 + 2HNO_3,$$

which does not account for the presence of phosphoric acid in

the filtrates; but if (4) and (5) are coupled, the precipitate will have the composition $Ag_5H(PO_4)_2$ which was obtained in the four cases previously quoted, the production of which can be expressed by the equation

(7) $$2Na_2HPO_4 + 5AgNO_3 = \underset{\overset{\uparrow}{Ag_3PO_4.Ag_2HPO_4}}{Ag_5H(PO_4)_2} + 4NaNO_3 + HNO_3.$$

For an expression which would account for the presence in the filtrate from the complete (?) precipitation of the silver, of both nitric acid and of phosphoric acid the following is suggested:

(8) $4Na_2HPO_4 + 6AgNO_3 = 2Ag_3PO_4 + 4NaNO_3 + HNO_3 + H_3PO_4$

It would appear then that the reaction between silver nitrate and disodium orthophosphate takes place in several distinct stages, and that the formation of a phosphate containing about 76 per cent. of silver is the most constant resultant. Also that free nitric acid and phosphoric acid remain in the solution from which no further precipitate can be obtained on the addition of the nitrate. It is our intention to further investigate this matter specially as regards the quantitative composition of these filtrates with a view to determining whether or not the last six equations suggested (Nos. 3 to 8) adequately express the reaction.

THE CHEMICAL LABORATORIES,
THE UNIVERSITY OF TORONTO.

UNIVERSITY OF TORONTO STUDIES

PAPERS FROM THE CHEMICAL LABORATORIES

No. 74: SOME ESTERS OF ARSENIOUS ACID, BY W. R. LANG, J. F. MACKEY AND R. A. GORTNER

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CXXX.—*Some Esters of Arsenious Acid.*

By William Robert Lang, John Francis Mackey, and Ross Aitken Gortner.

J. M. Crafts (*Bull. Soc. chim.*, 1870, [ii], **14**, 99), in referring to the existence of compounds of arsenic with alcohol radicles, pointed out that no esters of arsenious or of arsenic acid had been prepared up to the year 1870, and described a method by which he obtained ethyl, methyl, and amyl arsenates; this consisted in heating the corresponding iodides in sealed tubes at 100° with normal silver arsenate. The esters were purified by washing with ether and distilling under diminished pressure. They are liquids of high boiling

point, above 200°, and suffer partial decomposition if distilled under atmospheric pressure; in the case of the amyl arsenate so much so that he found it impossible to obtain it pure even when distilled in a vacuum. The addition of water to them causes immediate and complete decomposition into arsenic acid and the alcohol. Crafts determined their composition by weighing the precipitated arsenic acid as the magnesium salt and the carbon and hydrogen by combustion, and gave them the formula R_3AsO_4. For the arsenites of the alkyl radicles he used three methods, a sealed tube being employed: (1) the interaction of arsenious oxide and ethyl silicate at 200°, (2) the interaction of ethyl iodide and silver arsenite at 150°; and (3) the interaction of arsenic bromide and sodium ethoxide, which last method he considered the best, although in it a secondary reaction between the ester formed and the sodium ethoxide causes a condition of equilibrium to be set up, and no more ester is formed.

It is to be noted that even if disodium hydrogen arsenite is employed the resulting arsenite is always the trialkyl salt. Crafts states that arsenious oxide and alcohol do not react when heated in a sealed tube, nor does arsenious oxide either with ether alone or with the addition of ethyl acetate, even when in contact for twenty hours.

These esters prepared by Crafts are specified by Auger (*Compt. rend.*, 1902, **134**, 238) as the only ones known, and he refers in a later paper (*Compt. rend.*, 1906, **143**, 907) to Crafts' inability to obtain any ester by heating the alcohols and oxides of arsenic in a sealed tube. Auger bases his conviction that an ester is produced on the fact that arsenious oxide is volatile in alcohol vapour, although not in water vapour, and concludes that this cannot be accounted for unless there is an ester formed.* Also he succeeded in preparing an ester from glycerol and arsenic oxide, and from ethyl, methyl, *iso*propyl, *iso*butyl, and *iso*amyl alcohols and arsenious oxide. He heated the alcohols with crystalline arsenious oxide for some hours, evidently in a sealed tube, as the temperatures quoted are far above the boiling points of the alcohols, and gives 6·5 per cent. as the extreme limit of esterification in the case of methyl alcohol, and 1·2 per cent. in that of ethyl alcohol. Calculating from his figures, the yield of ester for the higher alcohols appears to be 2·62 per cent., 0·25 per cent., 1·00 per cent., and 0·63 per cent. for propyl, *iso*propyl, *iso*butyl, and *iso*amyl alcohols respectively.

So far as can be gathered from the paper, Auger takes no account of the extreme solubility, as we have found, of arsenious oxide in the ester. These small yields and the difficulty found by Crafts in

* We have passed the vapour of methyl alcohol over arsenious oxide heated in a long tube, and the ether obtained differs entirely from methyl arsenite.

obtaining any results from the action of the acid on the alcohol are evidently due to the reversal of the reaction:

$$6ROH + As_2O_3 = 2R_3AsO_3 + 3H_2O \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Auger states that he removed the water as it was formed by fractional distillation (in the case of *iso*butyl and *iso*amyl esters), or by passing the mixture of alcohol and water vapour over calcium carbide placed in an adapter, thus removing the water and allowing the alcohol to drop back into the flask in which the reaction takes place. An excellent yield, how much is not stated, of propyl, *n*-butyl and *iso*butyl arsenites was thus obtained. Phenol, in the same way, yielded an ester hitherto only prepared by the action of sodium phenoxide on arsenic trichloride.

The nature of the reaction expressed by equation (1) and the properties of the ester clearly show that only by removing the water as it is formed can one expect to get a large yield. Our work has been done in two ways, namely, by heating the mixture in a vessel to which is attached a modified Soxhlet tube and condenser, the Soxhlet containing anhydrous copper sulphate, and by adding this dehydrating agent directly to the mixture. A comparison of the yields obtained is given in the sequel. By these two methods yields of from 14·8 per cent. (cold) to 58·6 per cent. (hot) have been obtained with aliphatic alcohols, and with the phenols as high as 90 per cent. Experiments have also been made, with very encouraging results, on benzyl alcohol and on esters of hydroxy-acids. We hope to show that the use of such a dehydrating agent as copper sulphate in a Soxhlet tube will allow of the preparation of a series of esters from the oxides and possibly sulphides of arsenic, antimony, tin, and perhaps bismuth with compounds containing hydroxyl, where the boiling points of such esters are higher than that of water, as, indeed, is the case with all of these; also with anhydrous copper sulphate in contact with the substances themselves. In many preparations, too, of esters generally and allied products, the formation of water in the reaction produces an equilibrium resulting in a very low yield. It is expected that by removing this water, as is done in the instances described in the present paper, the yields will be greatly increased in many commercial processes.

Experimental.

Heating with Inverted Condenser only.—Weighed quantities of propyl, *iso*butyl, and *iso*amyl alcohols were mixed with excess of arsenious oxide and heated with a direct flame for forty-five minutes in a flask to which a reflux condenser was attached. The clear liquid obtained was poured off from the excess of arsenious oxide and fractionated under diminished pressure. The esters so purified were

analysed and the yield compared with that calculated from equation (1).

Our method of ascertaining the composition of the esters differs from that used by Auger.* The ester was decomposed with water, forming arsenious oxide and liberating the alcohol. The arsenious oxide was dissolved in sodium carbonate and titrated with *N*/10 iodine (a preliminary test having shown that the alcohol did not react with iodine). By this means the quantity of arsenic in the ester was determined.

iso-*Amyl Arsenite.*—1·4 Grams were decomposed with 10 c.c. of water, sufficient sodium carbonate added to dissolve the arsenious oxide, and the whole diluted to 100 c.c.; 25 c.c. of this required 17 c.c. of standard iodine for oxidation, corresponding with 22·4 per cent. of arsenic. In 50 grams of the ester, the alcohol was determined and found to weigh 39 grams, or 78 per cent. *iso*Butyl and propyl arsenites were also analysed in a similar way:

Ester.	Per cent. As found.	Per cent. As calculated as $(RO)_3As$.
Methyl	44·5	44·6
Ethyl	—	—
Propyl	29·6	29·7
*iso*Butyl	25·7	25·5
Amyl	22·2	22·3
*iso*Amyl	22·4	22·3

Expressing these as salts of arsenious acid, the formulæ become $(C_5H_{11})_3AsO_3$, $(C_4H_9)_3AsO_3$, and $(C_3H_7)_3AsO_3$.

Propyl arsenite is a yellow, mobile liquid boiling at 216° and decomposing very readily on addition of water.

iso*Butyl arsenite* is a deep yellow, mobile liquid of specific gravity 1·069; it decomposes rapidly in presence of water into *iso*butyl alcohol and arsenious oxide; under 760 mm. pressure it decomposes at 242°, and boils at 157° under 30 mm. pressure.

iso*Amyl arsenite* is a yellow liquid of specific gravity 1·050; it boils at 185° under 30 mm. pressure, and under atmospheric pressure it decomposes at 284°; in the presence of water, it decomposes into *iso*amyl alcohol and arsenious oxide.

Heating with Soxhlet Attachment and Anhydrous Copper Sulphate.—To eliminate the water as it is formed and so increase the yield of ester, the conditions of the experiments were modified. One hundred and sixty grams of *iso*amyl alcohol were added to 70 grams of

* Auger determined the amount of arsenic in the cooled liquid obtained (a mixture of the ester and alcohol) by means of iodine. The difference between this and the amount of arsenious oxide that would dissolve in the same quantity of alcohol in the cold was taken as representing the amount of ester formed (*Compt. rend.*, 1906, **143**, 908). No account was taken of the solubility of arsenious oxide in the esters themselves.

arsenious oxide in a 300 c.c. flask. An ordinary Soxhlet tube was connected with the flask, and a condenser, fitted with a calcium chloride tube, was attached to the Soxhlet, which contained a large filter paper filled with anhydrous copper sulphate. The liquid in the flask was heated to boiling, and the water formed was absorbed by the anhydrous copper sulphate, which turned blue as soon as the first drops of condensed liquid fell on it. Heating was stopped after forty-five minutes, when small rings of a compound of high boiling point began to form on the sides of the flask; after cooling, the clear product was filtered and fractionated under diminished pressure. 110·25 grams of ester were obtained, being a yield of 58·6 per cent. as compared with 13·22 per cent. obtained without the use of a dehydrating agent.

In similar experiments with *iso*butyl and propyl alcohols, yields of 56·25 per cent. and 56·75 per cent. respectively were obtained, as compared with 11·09 and 8·79 per cent. when no dehydrating agent was employed.

Use of Dehydrating Agent in the Cold.—The esterification of these three alcohols by arsenious oxide can be carried out even in the cold if a dehydrating agent is used; 120 grams of the alcohol were shaken in a stoppered bottle at room temperature with 60 grams of arsenious oxide and 70 grams of anhydrous copper sulphate for three days. The following yields were obtained: *iso*amyl arsenite, 17·2 per cent.; *iso*butyl arsenite, 15·8 per cent.; propyl arsenite, 14·8 per cent.

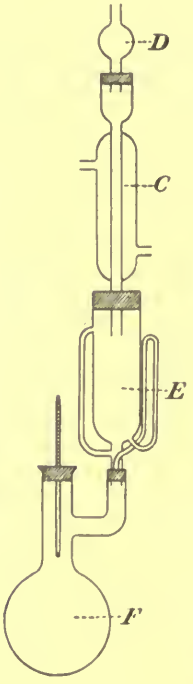
The following table indicates the comparative yields (per cent.) by different methods:

Ester.	Auger (in sealed tube).	Reflux condenser.	With anhydrous copper sulphate: in Soxhlet.	in the cold.
Methyl	6·5	—	33·8*	—
Ethyl	1·2	—	4·5*	—
Propyl.....	2·62	8·79	56·75	14·8
*iso*Butyl	0·25	11·09	56·25	15·8
Trimethylcarbinol	—	—	54·27	—
Amyl	1·00	—	54·00	—
*iso*Amyl	0·63	13·22	58·62	17·2

* The Soxhlet was not used, but the anhydrous copper sulphate was placed with the alcohol and arsenious oxide in a flask fitted with a reflux condenser.

A probable explanation of the low yield in the case of the ethyl arsenite lies in the fact that ethyl alcohol itself has a strong affinity for water which, for small quantities of water present, cannot be overcome by the anhydrous copper sulphate. This is readily shown by adding a drop of water to 5 c.c. of ethyl alcohol in which a little anhydrous copper sulphate has been placed. The copper sulphate is apparently not affected, whilst in the case of the higher alcohols a blue colour appears almost instantly, showing the hydration of the

copper sulphate. Methyl alcohol does not respond to this test as readily as do the higher alcohols, but it responds more readily than does ethyl alcohol. The yield in each case, using the copper sulphate, probably bears a direct relation to the respective affinities of the alcohol and of the copper sulphate for the water of the reaction. If a substance could be used which had a greater dehydrating power and at the same time was insoluble in alcohol, a higher yield would doubtless be obtained. Calcium carbide (Auger, *Compt. rend.*, 1906, **143**, 908) is not such a material: we have compared the yields obtained by replacing the anhydrous copper sulphate in the Soxhlet with fresh calcium carbide, using various alcohols, and the highest yield was in the case of *iso*amyl alcohol where 40·2 per cent. of ester was obtained after two hours' heating.



Esters obtained with Phenol and its Homologues.

For the esterification of these with arsenious oxide a side-necked flask was used the neck of which was bent upwards and attached to the Soxhlet, leaving the mouth of the flask free to receive a thermometer (see figure).

Phenyl Arsenite.—Weighed quantities of phenol (140 grams) and arsenious oxide (80 grams) were heated together, and in all cases it was observed that the reaction began at 100°, the mixture boiling violently at that temperature. The thermometer gradually rose to 133°, when a thick cloud formed in the flask. The temperature remained constant at that point for a few minutes and then gradually rose to a maximum, where it was kept for about five minutes: the heating was then stopped and the contents of the flask allowed to cool. The mixture of phenol, ester, and arsenious oxide, the latter of which is very soluble in the ester, was shaken with benzene, causing the precipitation of the arsenious oxide dissolved in the ester. The mixture was then filtered and the benzene solution of the ester fractionated under diminished pressure. The benzene distilled at 20°, the phenol at 69°, and the ester at 305°. The ester, purified by redistillation, weighed 105 grams, representing a yield of 60 per cent. *Phenyl arsenite* is a deep yellow, viscous liquid with a specific gravity of 1·59; it freezes at 31°, and boils at 305° under a pressure of 30 mm. It dissolves readily in methyl alcohol, benzene, ethyl acetate, or chloroform, and decomposes on addition of water, but not

so readily as the fatty arsenites. It was found on analysis to correspond with the formula $(C_6H_5O)_3As$, or $(C_6H_5)_3AsO_3$.

o-, m-, *and* p-*Tolyl Arsenites.*—One hundred grams of each of the cresols were heated with arsenious oxide for thirty minutes in the apparatus previously described, the arsenious oxide being separated by benzene. The liquid was then fractionated, and the esters, after having been purified and analysed as in the case of the phenyl arsenite, were found to correspond with the formulæ $(C_6H_4Me)_3As$, or $(C_6H_4Me)_3AsO_3$.

Naphthyl Arsenite.—One hundred grams of naphthol were heated with 30 grams of arsenious oxide for thirty minutes and the arsenious oxide in the ester separated by means of benzene. As yet, however, the pure ester has not been isolated.

Benzyl Arsenite.—One hundred grams of benzyl alcohol were heated with 35 grams of arsenious oxide for thirty minutes. The maximum temperature was 240°. The clear liquid was decanted and 75 c.c. of benzene added, the arsenious oxide collected, and the filtrate fractionated under 30 mm. pressure. The *benzyl arsenite* distilled at 285°, suffering partial decomposition. Although in the case of the fatty alcohols a drying agent in the Soxhlet was essential to absorb the water formed and to allow only the alcohols themselves to drop into the mixture, no such device was necessary with the phenols, as practically no phenol or ester ever found its way further than the side tube of the Soxhlet. The water formed remained in this apparatus, there being never sufficient volume of liquid produced to cause the syphon attachment to come into play.

To ascertain if it was possible to obtain these esters without the removal of the water formed during the reaction, the same quantities of phenol, benzyl alcohol, *o*-, *m*-, and *p*-cresol respectively, as were used in the previous experiments, were heated with arsenious oxide in a flask fitted with a reflux condenser only, but in no case was any arsenite formed in quantities sufficient to enable it to be isolated.

Method of Analysis for Esters of Phenol and its Homologues.—To determine the composition of the esters, it was found necessary to distil them several times in order to remove all traces of arsenious oxide which is readily soluble in them, in some cases to the extent of 30 per cent. About 3 grams of the ester were decomposed by 5 c.c. of water and 10 c.c. of potassium hydroxide (containing 700 grams of potassium hydroxide per litre), and the whole diluted to 500 c.c. Two samples of 10 c.c. each were taken for analysis; to one sample standard iodine was added in excess, shown by the formation of a precipitate of tri-iodophenol and the appearance of a clear yellow solution, the temperature being kept at 65°. The mixture was then cooled, acidified with sulphuric acid, and diluted to 500 c.c. with

water. The excess of iodine in 100 c.c. of this was titrated against standard thiosulphate, using starch as indicator. The quantity of thiosulphate necessary, multiplied by five, represents the quantity of iodine used. This quantity, subtracted from the original amount of iodine added, gave the amount necessary to change both the phenol to tri-idophenol and the arsenious oxide to arsenic oxide. To determine the quantity of arsenious oxide present in the ester, an excess of standard potassium dichromate was added to the second sample and this excess was determined with standard ferrous sulphate. The ratio between the dichromate and iodine being known, the number of c.c. of iodine equivalent to the amount of dichromate used was found and subtracted from the total iodine obtained in the previous determination, the difference being the amount combined with the phenol. From these data the relative quantities of arsenious oxide and phenol, formed by decomposing the ester, were obtained, and the composition of the ester thus determined.

To test the accuracy of this method, estimations were made with weighed quantities of (*a*) phenol, (*b*) arsenious oxide, (*c*) a mixture of these.

(*a*) To 0·8826 gram of phenol, 5 c.c. of potassium hydroxide (700 grams per litre) were added and the whole diluted to 250 c.c. . .(1)

Ten c.c. of this solution were found to be equivalent to 25·75 c.c. of standard iodine.

(*b*) To 0·5 gram of arsenious oxide, 5 c.c. of the same potassium hydroxide were added and diluted to 250 c.c. . . . . (2)

Ten c.c. of this solution were found to be equivalent to 6·5 c.c. of standard iodine.

(*c*) To 10 c.c. of solution (1), 10 c.c. of solution (2) were added and found to require 32·30 c.c. of standard iodine.

Thus 10 c.c. of solution (1) required 25·75 c.c. of iodine, and 10 c.c. of solution (2) required 6·50 c.c. of iodine; in all 32·25 c.c. as compared with 32·30 c.c. when mixed, a difference which is well within the limits of experimental error.

In order to see if arsenious oxide can be determined accurately in the presence of phenol by means of dichromate, experiments similar to those made with iodine were carried out with it. Ten c.c. of solution (2) required 6·07 c.c. of dichromate, a mixture of 10 c.c. of (2) with 10 c.c. of (1) required 6·09 c.c. of dichromate, or an error of less than 0·3 per cent.

Properties of the Arsenites prepared from Phenol and its Homologues.

	Phenyl arsenite.	Benzyl arsenite.	*o*-Tolyl arsenite.	*m*-Tolyl arsenite.	*p*-Tolyl arsenite.
Yield (per cent.)					
(*a*) with Soxhlet	60	100	96	94	95
(*b*) without Soxhlet	nil	nil	nil	nil	nil
Specific gravity	1·59	1·43	—	1·45	1·46
Refractive index *	—	1·572	—	—	—
Boiling point † under 30 mm..	305°	255°	—	346°	—
Freezing point.....	− 31°	− 36°	—	—	—
Colour	yellow	blue	dark brown	dark brown	brown

* The blanks indicate that the refractive index is greater than 1·62098, the limit of the prism used.

† Where the boiling point is not given it is above 360°.

All these esters are soluble in methyl and ethyl alcohols, ether, benzene, ethyl acetate, or chloroform, and are decomposed at once by water.

This method of esterification is being carried out with arsenious oxide and the dihydric and trihydric phenols, but the quantitative results are not yet ready. A successful attempt has also been made to form similar esters with hydroxy-acids, methyl salicylate being heated with arsenious oxide. The products of the reaction, namely, water and an oil, were driven up into the Soxhlet where the latter decomposed, liberating arsenious oxide. The oil boils at about the same temperature as the methyl salicylate and has an almost unbearable odour. When the dehydrating agent is used in the Soxhlet it is expected the new ester will readily be separated.

Experiments have also been tried with arsenious sulphide in place of the oxide and a small yield of an ester obtained, presumably of the composition R_3AsS_3, but the upper portions of the flask and the condenser became coated with the orange-coloured arsenious sulphide, showing that decomposition had occurred. The work is being continued.

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CII.—*The Volumetric Estimation of Silver.*

By William Robert Lang and John Obins Woodhouse.

In this journal (Lang and Allen, Trans., 1907, **91**, 1370) there was described an apparatus for the estimation of sulphates and salts of barium based on the rapid clearing of turbid solutions in narrow tubes. The same apparatus was used to determine silver by standard sodium chloride with a view to improving on the well-known Gay-Lussac method, but great difficulty was experienced in determining the end-point, the silver solutions not clearing sufficiently rapidly. The

apparatus was therefore modified considerably, with the result that estimations of silver were done in half an hour with an average error of less than a-tenth of one per cent.

The principal differences from the former apparatus were the use of fine sand to retain the silver chloride precipitate, the replacement of the funnel by a short piece of thin-walled glass tubing, which enables the slightest opalescence to be easily observed, and the permanent attachment to an exhaust for washing the precipitate and solution down the tube.

A rubber cork, pierced with two holes, is inserted in a flask, *A*, of about 600 c.c. capacity. Through it passes a tube, *C*, of about 60 mm. diameter, fitted with a stopcock, *D*, and to its upper end is sealed about 4 cm. of a thin test-tube, *E*, of 1—1·5 cm. diameter. About 8 cm. from the lower end of the tube *C*, a plug of glass-wool is inserted and the remainder filled with sand, previously washed free

from impurities. The sand is held in its place by a second plug of glass-wool, and the curved piece of tubing, *B*, filled with glass-wool and attached to *C* by a small piece of rubber tubing. The curved portion may, of course, be sealed on, but in these circumstances is not so readily filled. This prevents the back suction from displacing the sand. Through the second hole in the cork a small piece of tubing passes, connected by a length of rubber tubing, *F.M*, to a three-way tap, *H*. *J* is a small hand aspirator to force a portion of the contents of *A* up the tube *C* for titration in *E*, whilst *K* leads to the exhaust pump. It is advisable to have a space between the tap *H* and the water pump, as this ensures there always being a ready vacuum available the moment the connexion is made through *H* to the flask.

The first set of experiments was made with quantities of a solution of silver nitrate of known strength, using *N*/10 sodium chloride in excess as precipitant, and titrating back with *N*/10 silver nitrate. A portion of the silver solution, equivalent to 0·5 gram of silver, is

placed in the flask *A* and diluted to about 100 c.c. with distilled water, 50 c.c. of the *N*/10 sodium chloride solution is then run into the flask directly, and the whole heated to boiling to coagulate the precipitated silver chloride.

N/10 Silver nitrate is then run in directly to the solution and precipitate up to within a few c.c. of the calculated amount necessary. The rubber cork with its attachment is replaced and the three-way tap, *H*, opened, and air drawn through the solution for a few minutes. This materially assists the settling of the precipitate. The tap is adjusted, and by means of the aspirator, *J*, some of the liquid and precipitate forced through the layer of sand and glass-wool * into *E*, which it reaches in a perfectly clear condition, the silver chloride being completely retained by the sand. A drop of *N*/10 silver nitrate is added, when a precipitate is formed, varying in intensity with the excess of salt still present. The liquid and precipitate are then sucked and washed down into *A*, and, if the thickness of the precipitate justifies it, about 1 c.c. of the silver solution is added *directly* to the contents of the flask. The stopper is again inserted, and the operation of forcing the mixture up into *E*, titrating, and washing down again, continued until no change is visible in the clear liquid, when a drop of the silver solution is added. The thin walls of *E* render the faintest opalescence readily observable, more particularly if a corresponding glass tube containing distilled water be used for comparison. The results of the first set of experiments are as follows :

In each case, 50 c.c. of silver nitrate solution were employed (= 0·5 gram Ag) and 50 c.c. of a solution of sodium chloride added, each c.c. of which is equivalent to 0·01081 gram Ag. This corresponds with 50·0463 c.c. *N*/10 sodium chloride. On titrating back and calculating the amount of silver equivalent to the nett sodium chloride used by the sample, the errors varied from zero to + 0·54 per cent. Each titration required twenty minutes.

In order to reduce this error, if possible, samples containing 1 gram of silver were taken, 100 c.c. of sodium chloride added (1 c.c. = 0·01081 gram Ag), and the excess titrated back with *N*/100 silver nitrate solution (table I).

As in analyses of silver alloys by Gay-Lussac's method, the precipitation is effected in the presence of free nitric acid, a series of experiments was carried out to ascertain the effect of varying proportions of acid. The volume of the solution containing 1 gram of silver was 100 c.c.; the amount of acid varied from 10 c.c. to 50 c.c., and the resulting errors from + 0·094 to − 0·216 per cent., the mean error being − 0·0634 per cent., the presence of the nitric acid thus tending to make the precipitation more complete.

* Glass-wool and asbestos were found to be incapable of retaining the precipitate.

TABLE I.

Grams Ag employed.	$N/100$-$AgNO_3$ used to titrate back, in c.c.	Nett $N/10$-NaCl used, in c.c.	Equiv. to grams Ag.	Diff. in Ag found, in grams.	Error per cent.
1·0	72·00	92·8926	1·0032	0·0032	+0·32
1·0	76·20	92·4726	0·9987	0·0013	−0·13
1·0	75·05	92·5876	0·99994	0·00006	−0·006
1·0	73·20	92·7726	1·0019	0·0019	+0·19
1·0	72·30	92·8626	1·0029	0·0029	+0·29

Average error = +0·266 per cent. and 0·068 per cent. Mean error = 0·198 per cent.
Average time taken = 27 minutes.

To test the usefulness of this apparatus as applied to the practical estimation of silver in bullion, the usual conditions under which this is done by the Gay-Lussac method were adhered to, namely, 1 gram of pure silver dissolved in about 15 c.c. of nitric acid, 100 c.c. of $N/10$ sodium chloride added, and the excess titrated with $N/100$ silver nitrate. (When necessary, any excess of silver solution added was titrated with $N/100$ sodium chloride.)

The following table contains the results of these experiments, and the time taken:

TABLE II.

Grams Ag employed.	$N/100$-$AgNO_3$ used to titrate back, in c.c.	Nett $N/10$-NaCl used, in c.c.	Equiv. to grams Ag.	Diff. in Ag found, in grams.	Error per cent.
1·004	72·00	92·8926	1·0032	0·0008	−0·08
1·000	73·30	92·7626	1·0018	0·0018	+0·18
0·9994	74·75	92·6176	1·00027	0·00087	+0·087
1·0018	73·80	92·7126	1·00129	0·0005	−0·05
1·0034	73·00	92·7926	1·0021	0·0013	−0·13
1·0030	72·30	92·8626	1·0029	0·0001	−0·01
1·0035	72·30	92·8626	1·0029	0·0006	−0·06

Average error = −0·066 per cent. and +0·133 per cent.
Mean error = −0·067 per cent. Average time taken = 30 minutes.

It may be added that no excessive shaking up of the mixture is required other than sufficient to ensure proper mixing after each addition of the reagent.

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CONCEPTIONS OF MATTER:—ANCIENT AND MODERN.

THE science that deals with the constitution of matter has occupied the time and energies of countless generations of men since the time of Adam, who, possibly, was himself an alchemist, as one might be led to believe when he reads of

> "A book where Moses and his sister,
> And Solomon have written of the art."(1).

The quest of the alchemist was the production of new substances and the conversion of one form of matter into other forms by a process of transmutation. This was possible, he argued, because, in nature, plants and animals were seen to grow, change, develop, and die, and that therefore the same growth and development ought to proceed in the mineral kingdom. Just as a grain of seed in the ground died, and from its dead body arose the perfect plant or tree, so, in the earth, the metals were looked upon as undergoing a growth and becoming more perfect—in time reaching the highest stage of all, namely, gold.

Alchemy did not give place to chemistry proper until the eighteenth century, and, in its long life, experienced many vicissitudes. Its students and followers were not merely natural but also moral philosophers; they regarded nature from both standpoints, watched and studied the course of nature as exemplified by the growth of living things, vegetable and animal, endeavoured to discover the secret of her workings, and trusted to be able to apply this secret to the transmutation of the baser into the nobler metals, to the production of an *Elixir Vitae*, which would be the cure of all ills, and, as a result of this, hoped for the mental happiness which would follow from the practical knowledge of the supreme secret of nature. Their quest was for an undefinable something, called by various writers *"the one thing," "the philosopher's stone," "the essence," "the soul of all things,"* and by many other names.

(1) *The Alchemist*: by Ben Jonson, 1610.

Though some alchemists believed in the power of this "essence," (which was presumed to have a dual nature, material and spiritual), to create things, yet the best writers seem to have had a real belief in the Supreme Being as alone having power to create and destroy; they hoped only to make one form of matter into a different form, not to create it. That this could be done they believed implicitly, and a simple illustration will show in how far their belief was justified. The mineral galena, which is a sulphide of lead containing some silver, has somewhat the appearance of the metal lead itself. This, when subjected to treatment, yields lead; and the lead in turn, on heating and removing the "calx," or earthy material formed, disappears, leaving a small portion of the precious metal silver. The alchemist took no consideration of the relative *quantities* of original material and the residual silver obtained: he used his results to confirm his preconceived theory of the transmutation of the baser metal, and did not, as would have been more logical, deduce a theory from his experimental results. The alchemist's belief remained firmly fixed in his mind, was a part of his system of ethics, indeed, not only from the example just given but from his observation of nature. That lead could not, by one wave of the alchemistic wand, be converted at once into gold he quite understood; a series of purifications, of "trying in the fire," was required before the perfect metal was obtained. In *The Alchemist* this view is expressed in these lines:—

> Nor can this remote matter suddenly
> Progress as from extreme unto extreme,
> As to grow gold, and leap o'er all the means,
> Nature doth first beget the imperfect, then
> Proceeds she to the perfect.

It was a far cry from the earlier alchemist to the chemists of the nineteenth century, or to the time when the ideas of transmutation had to give way,—thanks to Priestly, Lavoisier, and others,—to theories evolved from the results of careful investigation of the quantitative changes occurring during chemical operations. The enunciation of Dalton's hypothesis of atoms placed chemistry on a new basis, and was the commencement of an era of phenomenal progress in chemical science. According to this theory, matter is composed of combinations of the atoms of elementary substances with one another, which unite together, by reason of their chemical affinity, to form molecules of new

substances. Matter, therefore, is composed of minute indivisible particles of the same or of different elements, and of these everything that is apparent to the senses is made up. Cut and carve down these particles as you may, in the end there is left the uncuttable particle or atom of each element.

This hypothesis of Dalton's was by no means new; indeed he merely resuscitated a theory put forward more than two thousand years previously. These early philosophers—Democritus (B.C. 460), Lucretius, the Latin poet who was born about a century before the Christian era—attempted to connect the differences of size, shape, and qualities of various forms of matter with the differences of size, shape, position, and movements of what they termed the *atoms* of matter. Everything material, they held, was composed of "a coalescence of certain unchangeable and indestructible particles"; no atom of anything could either be created or destroyed; when substances ceased to exist, another was formed; no destruction of matter took place, merely a rearrangement of the atoms. The ancients were evidently as fully alive to the soundness of the doctrine of the indestructibility of matter as we are now. Their conception of its various forms coincides with the modern ideas also; a solid body consisted of a vast number of atoms squeezed closely together, a liquid of a less number more loosely connected, and a gas of a still smaller number able to move freely and distributing themselves uniformly throughout the space containing them.

The atomic theory, as enunciated by the Manchester schoolmaster (Dalton), was based on observations of the manner in which the elements combined with one another, namely in fixed and definite proportions:—the atoms of each element had a definite weight peculiar to all the atoms of that particular substance. This theory has served the purposes of chemists for the past century, and has been, and still is a convenient quantitative method of expressing chemical changes as they occur. The chemist can calculate the amounts of material necessary for the formation of new combinations—alike in the factory as in the laboratory—and can prophesy the yield he will obtain from the union of known quantities of different elements or compounds. But though the atomic theory has for so long been a perfect working hypothesis from the chemist's point of view, recent researches, depending mostly on the study of electricity and radio-activity, have led to the displacement of the atom from its position as the unit form of matter. The

atom is slowly but surely being proved to consist of an aggregation of still smaller units, (electrons, corpuscles or ions,—call them what you will) incapable of detection by ordinary chemical methods, but readily recognisable by the physicist, on account of their influence in rendering dry air a conductor of electricity. Professor J. J. Thomson, of Cambridge, claims to be able to detect with certainty, by electrical methods, quantities of radio-active substances less than one hundred-thousandth part of the least quantity which the chemist could detect by any method of analysis known. He stated in his lectures delivered at Yale College, some eighteen months ago, that the quantity of these radiations which could be detected electrically were to the quantity of any known element (so-called), which could be detected by ordinary chemical analysis, in the proportion of a second to a thousand years!

Since the discovery of the Röntgen rays, in 1895, the properties of emanations from the mineral substances uranium, thorium, and radium, have occupied the attention of scientific investigators; and it is to them that we owe the new ideas and conceptions of matter as capable of existence in even a more attentuated condition than the atom. From phenomena connected with the emission of rays and emanations from these radio-active bodies, it is evident that they consist of particles infinitely more minute than atoms. The emission of atoms themselves seems quite intelligible, as matter, in many forms, can evaporate, and some substances emit a perfume, if not always appreciable to human beings, certainly to the lower order of animals. No one has seen a smell, nor the wind, nor the minute particles worn away from a pavement, yet no one doubts the existence of these particles. But, in the case of the emissions from radio-active bodies, their speed is found to be enormous, and their atomic weight something like one-thousandth of the atomic weight of hydrogen. The atom of matter must therefore be considered as complex, not simple, and composed of a number of smaller bodies interleaved and interlocked, and in a state of rapid motion. Occasionally an atom loses one of these minute constituent parts, which becomes separated from it, chipped off, as it were, and which flies away at a speed which Sir Oliver Lodge has calculated as being many thousand miles a second: these portions thus separated are known as the α rays. But this rupture of the atom is immediately followed by a further splitting off of other parts of it, which are so minute as to be

able to penetrate through solid bodies; and yet a third or ethereal emanation, called the γ rays, follows as a consequence of the break up of the atom. What, then, are these minute portions which the experimental physicist can recognise, handle and investigate? They may be called the corpuscles, or electrons, and are of the order of many thousandths of the magnitude of an atom of matter, which is commonly estimated as being about one fifty-millionth of an inch in diameter. Sir Oliver Lodge has given an illustration of the size of these corpuscles by asking one to imagine an atom of matter magnified to the size of an ordinary church, when its constituent ions would be represented in size by this full stop.

This research into these striking but obscure forms of radiation has laid the foundation of a new hypothesis regarding the constitution of all matter. The phenomena of radio-activity have been found not to be confined entirely to the elements uranium, thorium, etc., which possess this property to a remarkable degree, but to be common to a great number of things, possibly to all things material. It has been found that certain mineral springs are radio-active; rain, snow, hail, the air of cellars, and the air contained in many soils, possess the same properties: the atmosphere itself has been shown to exhibit this property, the experiments leading to this result having been made in our own Physical Department by Professor McLennan and his assistants. Indeed, it might be said that corpuscles or electrons are everywhere about, incessantly streaming from the earth, from the ends of branches, from rails, from telegraph poles, and from the sun itself. These particles, too, are all of the same nature, size and kind, no matter from where they may come; and it seems likely that they constitute the primordial form of matter, various combinations of which, interlocked together, go to make up what, up to now, have been looked upon as the elements, of which some seventy or eighty are recognised by chemists. And does this mean that the ancient alchemists were not so very far wrong after all in their belief that one form of matter could be converted or transmuted into another? It seems so, for, in experiments conducted in London by Sir William Ramsay, the emanation from radium was found to have lost its characteristics on standing for a week, and to have developed the properties of a known elementary substance, the gas helium! The radium emanation had become destroyed,

altered,—degenerated, one might call it,—into another form of matter entirely!

What interpretation, then, can be put on these results regarding the fundamental constitution of all material things? The existence of bodies infinitely smaller than the smallest atom, has been clearly demonstrated, and, for many reasons, it has been concluded that they are akin to electricity. Sir Oliver Lodge holds that electricity possesses two of the fundamental properties of matter, namely mass and inertia; light and electricity have been shown to be closely allied to one another in their mode and speed of propagation. Is electricity matter and is matter electricity? Evidently they are closely related, and if the corpuscles or electrons emitted are not electricity, they at least are the carriers of electricity. The new conception of matter seems to indicate that it and electricity are one and the same thing, and that the chemist's atoms consist of systems of positive and negative electrons, and of nothing else. If the simplest atom, that of hydrogen, consists of, say, 350 positively and 350 negatively charged electrons, interleaved together and in a state of violent motion within themselves, then some sixteen times as many constitute the atom of oxygen, and other multiples of this, the atoms of other elements.

W. R. Lang.

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BY R. J. MANNING AND W. R. LANG.

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THE ESTIMATION OF BORIC ACID AND BORATES IN FOODSTUFFS AND COMMERCIAL PRODUCTS.

BY R. J. MANNING AND W. R. LANG.

In a previous paper (Manning and Lang; this J., 1906, 397), a new method of estimating boric acid was described, which was found to give results in some cases to within 0·05% of the theoretical. Since the completion of this work the method has been used in the University Laboratory of Applied Chemistry and pronounced satisfactory. Its application to the determination of borates in such articles as milk, common salt, etc., is the object of this present paper, these substances being found to contain small quantities of boric acid in some form or other.

The results of this investigation are now given arranged as follows:—

(1) Two methods for the determination of borates in milk.

(2) Two methods for their determination in common methylated spirits.

(3) Two methods for their determination in commercial common salt.

Estimation of Boric Acid in Milk.

Method I.—Distillation and precipitation as barium borate.—This method is almost exactly similar to that previously published (*loc. cit.*), only, of course, adapted to the needs of the case. The first precaution necessary was to obtain milk absolutely free from boric acid and borates. About 300 c.c. of pure milk was introduced into a distilling flask and some boric acid dissolved in it, or else it was introduced in the alcohol, of which 400 c.c. were at first taken. Additions of more alcohol were made from time to time to ensure the complete distillation of the tri-ethyl or tri-methyl borate. It was now found that no matter how much boric acid was introduced in the milk that no precipitate whatever of barium borate was formed. In order to have the tri-methyl borate formed the introduction of sulphuric acid was necessary. A long series of experiments were therefore undertaken to determine what amount of sulphuric acid was necessary

with 300 c.c. of milk, as a result of which it was found that at least 70 c.c. of concentrated sulphuric acid are necessary; the large amount of water in the milk decomposes the tri-methyl compound into boric acid and alcohol. In this case the boric acid will distil over only at a very high temperature. The sulphuric acid appears to prevent this decomposition. After distilling for half an hour, the distillate was treated with a few drops of a concentrated solution of barium chloride. At this stage a slight precipitate sometimes occurred. The fats in the milk contain three esters, those of palmitic, stearic, and oleic acids. These all form compounds with barium chloride which are insoluble in water and in cold dilute hydrochloric acid. It was found that if the temperature in the distilling flask rose about 80° C., a small portion of these (probably oleic acid) was carried over. Therefore, on the addition of barium chloride, a flocculent precipitate of barium oleate appeared. This had to be removed by filtration before the experiment could be proceeded with. The distillate was now titrated against a freshly prepared concentrated sodium hydroxide solution, prepared, as before described, by dissolving newly cut pieces of sodium in water in a silver dish; phenolphthalein was used as indicator. Care had to be taken to guard against overstepping the neutral point, as the excess of the alkali united with the barium chloride to form the hydroxide. The precipitate of barium borate was now filtered off on a tared filter paper, washed carefully with alcohol, dried at 110° C., and weighed.

First of all a test series was made in order to see how small a quantity of boric acid would, on neutralisation of the distillate, give a precipitate distinctly seen by the naked eye. To this end, 50, 40, 30, 20, 10 parts boric acid were introduced into 10,000 parts of milk. The precipitate of 50 parts boric acid in 10,000 parts milk was quite heavy, the 40 less so. In this manner a gradation was obtained until when 10 parts in 10,000 was reached only a faint milkiness was obtained. This last was repeated several times with precisely the same result. Below this point traces of precipitate became untrustworthy, especially as a trace of boron compounds could be obtained from impure methylated spirits. This, however, will be dealt with later.

The results obtained from weighed precipitates were :—

Boric acid introduced.	Barium borate.	Yield.
grms.	grms.	Per cent.
1·50	2·6890	99·5
1·50	2·6830	99·3
0·50	0·8941	99·25
0·15	0·2649	98·0
0·12	0·1970	91·1
0·09	0·1414	87·2
0·06	0·0879	81·3
0·03	0·0340	63·33

Method II.—Distillation and titration.—Instead of precipitating the boric acid from the distillate as in Method I., the distillate was diluted with water up to one litre. Portions of 100 c.c. were neutralized with $N/10$ potassium hydroxide in presence of phenolphthalein. About 30 c.c. of glycerin were then added, and the titration continued until a permanent shade of pink was obtained.

Boric acid introduced.	Yield.
grms.	Per cent.
1·50	99·6
1·50	99·5
0·50	99·47
0·15	98·43
0·12	92·1
0·09	88·7
0·06	83·0
0·03	69·2

Method III.—The milk was first evaporated and afterwards charred. The charred mass was then treated with water and titrated in the presence of glycerin against potash, using phenolphthalein as indicator. The method is not yet complete and the results are temporarily withheld.

Estimation of Borates in Methylated Spirits.

Method I.—By distillation and precipitation.—The method was exactly similar to that used in the case of milk; 300 c.c. of methylated spirits and 25 c.c. of concentrated sulphuric acid were distilled until the temperature rose to 75°, when the boron compound was precipitated by barium chloride and weighed as before. One litre of methylated spirits was found to contain 0·0183 grm. boric acid as a borate of some sort.

Method II.—By distillation and titration.—Owing to the exceedingly small amounts of boric acid in the alcohol it was very difficult to obtain results that agreed. The large distillate was diluted to a known volume (500 c.c. usually), and portions of 100 c.c. taken out at a time and titrated against $N/10$ potassium hydroxide with 30 c.c. glycerin and a few drops of phenolphthalein. One litre of methylated spirits was found to contain 0·0160 grm. boric acid.

Estimation of Borates in Salt.

Method I.—By Distillation and Precipitation.—A weighed amount of common packing salt (preferably about 5 grms.) were dissolved in the necessary amount of concentrated sulphuric acid. This salt solution was now introduced with 300 c.c. of methylated spirit into a distilling flask. From this point on, the experiments were exactly similar to the previous ones. From the estimations it was found

that 100 grms. salt contain 0·88 grm. of boric acid as a bor te

Method II.—By Distillation and Titration.—Instead of precipitating the boric acid as barium borate, it was titrated against $N/10$ potassium hydroxide in the usual manner. 100 grms. of packing salt were found to contain 0·874 grm. of boric acid as a borate.

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No. 60: The rate of oxidation of arsenious acid by chromic acid, by RALPH E. DELURY 0.25

No. 61: The induction by arsenious acid of the reaction between chromic and hydriodic acids, by RALPH E. DELURY ..

No. 62: The detection and estimation of α-naphthoquinone, β-naphthoquinone, phthalonic acid and phthalic acid, by MAITLAND C. BOSWELL 0.25

No. 63: The deteriorating effect of "acid pickle" on steel rods, and their partial restoration on "baking," by HERBERT A. BAKER and Professor W. R. LANG 0.25

No. 64: The oxidation of naphthalene to phthalonic acid by alkaline solutions of permanganate, by R. ARTHUR DALY 0.25

No. 65: The reaction between bromic, hydriodic and arsenious acids, by FRED. C. BOWMAN 0.25

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No. 67: The experimental data of the quantitative measurements of electrolytic migration, by J. W. MCBAIN 0.25

No. 68: The estimation of boric acid and borates in foodstuffs and commercial products, by R. J. MANNING and Professor W. R. LANG 0.25

No. 69: A new type of catalysis, the acceleration by chromic acid of the reaction between bromic and hydriodic acids, by ROBERT H. CLARK 0.25

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THE DETERMINATION OF BORIC ACID, ALONE AND IN THE PRESENCE OF PHOSPHORIC ACID.

BY

RODGER J. MANNING AND WILLIAM R. LANG.

LONDON:

VACHER & SONS, WESTMINSTER HOUSE, GREAT SMITH STREET, WESTMINSTER, S.W.

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1906.

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Canadian Section.

Meeting held at Toronto, on Friday, April 6th, 1906.

DR. F. J. SMALE IN THE CHAIR.

THE DETERMINATION OF BORIC ACID, ALONE AND IN THE PRESENCE OF PHOSPHORIC ACID.

BY RODGER J. MANNING AND WILLIAM R. LANG.

In a recent paper in this Journal, by Dr. Milton F. Schaak (1) on methods of estimating boric acid, mention is made of the compound formed by this acid and methyl alcohol in mixtures thereof, its distillation and collection over a weighed quantity of calcium oxide by which the ester is decomposed and the boric acid becomes fixed and, after ignition, is calculated by increase of weight (2).

Berzelius' method, used and recommended by Thaddeeff (3), depends on the formation of potassium borofluoride from the distilled trimethyl borate: its accuracy is, however, found to be doubtful owing to the imperfect insolubility of the compound (4). Other methods, such as that of Partheil and Bose (5) and that of Mylius and Meusser (6), are pronounced "unsatisfactory," "complicated" and "tedious."

This paper deals primarily with the separation of boric acid as the trimethyl compound and its subsequent gravimetric estimation as the barium salt. The first series of experiments is connected with this, the second has reference to volumetric methods of estimating boric acid in the distillate, and the last deals with its direct titration in mixtures of other acids.

I.—In order to determine, first, if boric acid is completely expelled as the trimethyl salt by distillation, quantities of from 0·5 to 1·5 grms. of boric acid (7) were placed in a retort, 250 c.c. of methyl alcohol added and the mixture distilled at a temperature of from 66° to 67° C., when it was found that after distillation at this temperature for an hour the residue in the retort contained only a small proportion of boric acid and, after one and a-half hours, none could be detected.

The estimation of the boric acid, thus expelled as the trimethyl compound, with barium chloride solution was proceeded with. Known amounts of boric acid were dissolved in methyl alcohol (8), placed in a retort, and the

distillate allowed to mix with a concentrated aqueous solution of barium chloride. The trimethyl borate reacts with the water according to the equation—

$$B(OMe)_3 + 3H_2O = B(OH)_3 + 3MeOH.$$

The boric acid thus liberated reacts with the barium chloride to form barium borate and free hydrochloric acid in which the former dissolves. Caustic alkali was then added and the resulting precipitate of barium borate, $Ba(BO_2)_2$, washed with alcohol till free from all traces of chlorides, dried at 110° C. and weighed on a tared filter. The resulting weights of precipitate were in all cases too high and this was found to be due to the presence of barium hydroxide which was precipitated on concentrating the solution from filtration (9). The proceeding was then modified to obviate this, and the liberated hydrochloric acid in the reaction—

$$2B(OH)_3 + BaCl_2 = Ba(BO_2)_2 + 2HCl + 2H_2O$$

neutralised accurately by means of semi-normal sodium hydroxide with phenolphthalein as indicator. The use of this strong solution of sodium hydroxide—and also of barium chloride—was necessary to prevent the solution of part of the barium borate in water, in which it was found to be appreciably soluble. Weighing the precipitated barium salt gave results corresponding to 99·68 per cent. of the theoretical.

Being now fully satisfied with the accuracy of this method, determinations of the boric acid in pure borax were undertaken. Amounts of borax of about 1 grm. were weighed out, mixed carefully with from 20 to 30 c.c. of concentrated sulphuric acid and added to 350 c.c. of methylated spirit (8) contained in a retort. An excess of sulphuric acid was found to be necessary to prevent the reprecipitation of the salt by the alcohol. The mixture was then subjected to distillation at a temperature of from 65°—70° C. and it was found advisable to keep the bulk of the alcoholic solution approximately constant by leading into the retort from a distilling flask a further supply of spirit. About 30 minutes sufficed to carry over most of the boron compound, but results showed it to be necessary to continue the distillation much longer. A period of one and a half hours was therefore chosen as the best time for the operation. The determination of the boric acid was done as described previously, and a number of estimations showed that the borax could be estimated in this way with only a very small error.

Wt. of borax taken.	Wt. of $Ba(BO_2)_2$.	Percentage found.
0·9728 grm.	1·1262	99·0
0·9700 ,,	1·1270	99·4
0·9364 ,,	1·0900	99·6

The presence of any appreciable comparative amount of water in the retort is to be avoided, as the trimethyl borate would then be decomposed, yielding the alcohol and boric acid, which would not distil over; the result would then be too low.

This method was further applied to mixtures containing phosphates and sulphates in addition to borates with perfectly satisfactory results.

2. *Volumetric estimation with previous distillation.*—As boric acid can be titrated with standard sodium hydroxide in the presence of glycerine, and the end-points in the formation of sodium borate indicated by phenolphthalein, several determinations were tried after decomposing the borate in alcoholic solution with sulphuric acid. The apparatus used was the same as in the previous experiments: the distillate was collected in water, made up to a litre and aliquot portions taken for titration. To each portion thus taken it was found necessary to have about one-third of the bulk of the solution glycerine[10]. The results of the titration gave 99·75 per cent. of the boron compound, this error—0·25 per cent.—being considerably less than the literature on the subject would lead one to expect.

3. *Direct volumetric estimation in the presence of phosphates and sulphates.*—A mixture of a phosphate, a sulphate[11] and a borate were treated with decinormal sulphuric acid till acid to Methyl Orange, thus setting free phosphoric and boric acids. Decinormal sodium hydroxide was then run in until the solution was neutral to Methyl Orange, which was found only to indicate the end of the formation of the sodium dihydrogen phosphate; a still further amount of alkali had to be added before the solution began to react alkaline with phenolphthalein showing that the disodium compound had been formed[12]. The boric acid not being neutralised at once in aqueous solution by alkali, glycerine was then added, and the titration of the boric acid completed. The results are given below from which the accuracy of the method may be seen:—

Amounts of $Na_2B_4O_7,10H_2O$.	Amount formed by titration as above.	Per cent.	Error.
0·2390 grm.	0·2385 grm.	99·82	0·18
0·2990 ,,	0·2985 ,,	99·85	0·15
0·3824 ,,	0·3823 ,,	99·95	0·05
	Average	99·88	0·126

An error avoided here by titrating the solution previously with the sodium hydroxide till neutral or faintly alkaline, is the quantity of alkali of necessity absorbed by the water before the first trace of alkalinity is apparent. Experiments showed this to be an appreciable

amount: in the case of 50 c.c. alcohol and 50 c.c. water, 0·0016 grm. potassium hydroxide was required.

The authors intend applying these methods to the determination of boric acid in food stuffs.

(1) 1905, 609.

(2) See Gooch. Ann. Chem. J., 9, 23—33, and Montemartini Gazz. chim. ital., 28, 344—348.

(3) This J., 1898, 953.

(4) See (2) and (3).

(5) Ber., 1901, 3611.

(6) Ber., 1904, 397, and this J., 1904, 269.

(7) The composition of the boric acid employed—whether $B(OH)_3$, HBO_2 or $H_2B_4O_7$—was determined by estimating the amount of B_2O_3 contained in it. A weighed amount of boric anhydride, formed by fusing the boric acid to a clear glass, was dissolved in water and titrated against potash with phenolphthalein as indicator. A weighed amount of boric acid was also titrated against the same potash. Hence the percentage of B_2O_3 in the acid used was found. In these titrations—and all subsequent ones in the second part of this paper—25 to 30 per cent. of glycerine was used, as it is found that the neutralisation of boric acid by alkali cannot be done with any degree of accuracy except in the presence of glycerine or other polyatomic alcohol. (R. T. Thomson, this J., 1893, 432.)

(8) Ordinary methylated spirits (free from mineral oil) were found to act equally well.

(9) Pure sodium hydroxide was used, prepared from metallic sodium.

(10) See note (7). Also J. Amer. Chem. Soc., 1898, 288. The determinations were done before the above papers were noticed.

(11) The sulphate might have been omitted, as it took no part in the subsequent reaction.

(12) A strong solution of disodium hydrogen orthophosphate is slightly alkaline to phenolphthalein. Comparative experiments were made with varying amounts of a saturated solution of this salt and equal quantities of water; phenolphthalein added to each and decinormal potassium hydroxide added to the water till the shades of pink were identical:—

Phosphate solution in c.c.	Alkali required for 50 c.c. of water.
0·00	0·02 c.c.
0·50	0·06 ,,
1·00	0·08 ,,
2·00	0·09 ,,
3·00 made up	0·10 ,,
4·00 to 50 c.c.	0·11 ,,
5·00	0·12 ,,
6·00	0·12 ,,
7·00	0·12 ,,
8·00	0·12 ,,

For most solutions of this salt, therefore, a deduction of 0·1 c.c. would be the maximum correction necessary.

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DECEMBER 31, 1906.

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THE DETERIORATING EFFECT OF "ACID PICKLE" ON STEEL RODS, AND THEIR PARTIAL RESTORATION ON "BAKING."

BY

HERBERT A. BAKER AND W. R. LANG.

LONDON:

VACHER & SONS, WESTMINSTER HOUSE, GREAT SMITH STREET, WESTMINSTER, S.W

1906. (8758)

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1906. (8258)

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Canadian Section.

Meeting held at Toronto, on Thursday, October 25, 1906.

PROF. W. H. ELLIS IN THE CHAIR.

THE DETERIORATING EFFECT OF "ACID PICKLE" ON STEEL RODS, AND THEIR PARTIAL RESTORATION ON "BAKING."

BY HERBERT A. BAKER AND W. R. LANG.

It is the universal practice in wire manufacture to "pickle" the steel rods in order to remove the black scale of oxide before drawing them into wire. This has long been known to deteriorate the quality of the rods, but it has been found that, if the rods are "baked" at 250° F. for some hours after this treatment, they are in a great measure restored, and can then be drawn into wire. The following physical tests were made in order to find out quantitatively the amount of such deterioration and subsequent restoration of the rods. The work was done on samples taken in the different stages of the process of manufacture at the Imperial Steel and Wire Company's plant at Collingwood, Ontario, at the suggestion of the manager, Mr. J. A. Currie. Samples of three different coils of rods were taken in the following stages:—(1) Before treatment with acid; (2) after acid cleaning; (3) after rusting; (4) after lime coating; (5) after baking. Table I. shows the tensile strength, percentage elongation over 8 ins., and percentage contraction of the rods; the strength of the bath, time immersed, and time of baking are also given.

The tests were made with a Riehlé machine, by the kind permission and with the assistance of the staff in the Engineering Department, University of Toronto. It may be observed that the ultimate strength remains throughout the process as constant as can be expected of that kind of test. The percentage elongation over 8 ins. rather unexpectedly remains constant, but the sudden drop in the ability to contract to a small "neck," before breaking, occurs immediately after acid treatment, and remains practically constant until after "baking," when a marked recovery in this property occurs, the three rods agreeing well in this behaviour. It is important to note that on this property of "necking in," or contracting in area on stretching, depends the property of drawing well through

TABLE I.

	Strength in lb. per sq. in.			Elongation over 8 ins.			Percentage contraction.		
Rod	A	B	C	A	B	C	A	B	C
				per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
Before treatment	65,700	50,700	69,100	16	13	12	63	66	67
After acid cleaning	61,400	59,700	64,200	16	13	13	38	44	47
„ rusting	62,800	57,000	64,700	17	14	11	38	47	44
„ lime coating	65,700	59,700	67,000	16	14	—	37	47	41
„ baking	65,700	58,000	67,600	16	13	—	57	66	56

The strengths of acid used, at 100° C., were: A, 38 per cent.; B, 11 per cent.; and C, 10 per cent.; and the times of immersion in the baths: A, 1 hr.; B, 45 mins.; C, 1 hr. 10 mins. All the rods remained in the "baker" for about 4 hours.

the die, which is a conical hole in a block of tungsten steel.

This deterioration and recovery at the same stages in the process is also well shown in the following bending tests, which corroborate the contraction tests :—

TABLE II.

Bending tests on the rods.

	Before treatment.	After acid cleaning.	After rusting.	After lime coating.	After baking.
Rod A.	100	70	64	64	100
„ B.	100	60	56	57	99
„ C.	100	71	55	53	100

These figures are relative, of course, and express the ability to bend a certain number of times through a definite angle before breaking. They are the result of averaging eight or ten tests in each case. The highest number was taken as 100, and the rest calculated proportionately. The results show a break in the bending properties of the rod immediately after acid treatment, and a recovery after "baking," thus corresponding to the effect on the rods as indicated by the contraction tests.

Shearing tests were also made, but the differences were so small that no conclusions could be drawn from them.

An examination of the wires of different diameters drawn from these rods (correspondingly marked A, B, C) was also made in the same manner :—

TABLE III.

Tensile strength and percentage contraction of wires.

1. *Tensile strength.*

		Wires A.	Wires B.	Wires C.
	Diam. in.	lb. per sq. in.	lb. per sq. in.	lb. per sq. in.
(*a*)	0·175	72,900	93,700	93,700
(*b*)	0·142	112,600	113,900	113,900
(*c*)	0·112	117,300	122,400	122,400
(*d*)	0·091	—	138,400	131,000
(*e*)	0·072	137,000	150,000	150,000

2. *Percentage contraction.*

		per cent.	per cent.	per cent.
(*a*)	0·175	52.0	54	47
(*b*)	0·142	45·0	38	36
(*c*)	0·112	28·5	31	32
(*d*)	0·091	—	36	33
(*e*)	0·072	20·0	37	30

It will be observed that wires B and C have a higher tensile strength than wire A. Incidentally the increase of tensile strength on drawing out will be observed. The fall in contraction area percentage, as the diameter of the wires tested decreases, is not so great in B and C as it is in A. This means that these wires could probably be drawn through two more dies before annealing would be necessary, while wire A would, in all likelihood, stand no more drawing. Thus B and C appear to be the better wires. The only difference in the treatment of the rods was that rod A was cleaned in 38 per cent. sulphuric acid, while rods B and C were cleaned in 10 per cent. acid. They were all "baked" about four hours—longer than usual—and are probably restored as much as possible. The results indicate that strong acid causes an unnecessary amount of deterioration in the rod, and that only weaker acid should be employed.

Table IV. gives the comparative bending abilities of the wires: this also would indicate that wires B and C are the better.

TABLE IV.

Bending tests on the wires.

	Wire A.	Wire B.	Wire C.
Diam. in.			
(*a*) 0·175	91	100	100
(*b*) 0·142	90	97	100
(*c*) 0·112	89	100	83
(*d*) 0·091	—	100	80
(*e*) 0·072	86	100	94

Many superintendents of plants have attributed the deterioration to the presence of sulphur, knowing that sulphur renders steel "cold short." This appears to the authors to be highly improbable, as careful analyses show no difference in the sulphur content, which was 0·051 per cent. both before and after treatment. It seems much more probable that a "hydride" of iron is formed, as has often been suggested. Several tests confirmatory of this idea were obtained, but not sufficiently conclusive for present publication. The investigation is being continued.

UNIVERSITY OF TORONTO STUDIES

PAPERS FROM THE CHEMICAL LABORATORIES

No. 70: AN IMPROVED FORM OF APPARATUS FOR THE RAPID ESTIMATION OF SULPHATES AND SALTS OF BARIUM, BY W. R. LANG AND T. B. ALLEN

(REPRINTED FROM THE JOURNAL OF THE CHEMICAL SOCIETY OF LONDON, VOL. XCI.)

No. 71: A BENZENE MODEL ON ONE PLANE FOR LECTURE PURPOSES, BY W. R. LANG

(REPRINTED FROM THE JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, VOL. XXIX.)

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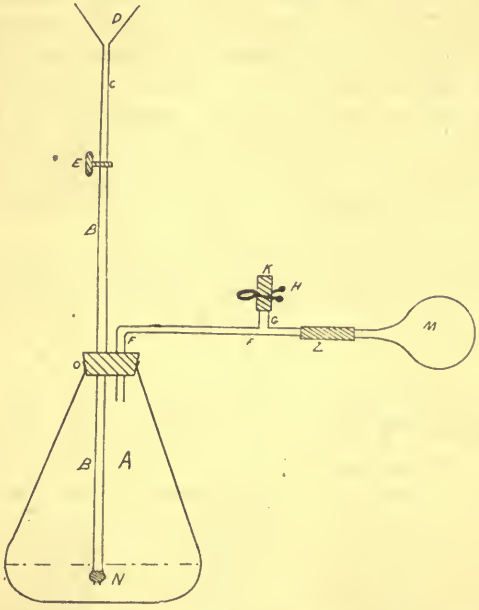
CXXVII.—*An Improved Form of Apparatus for the Rapid Estimation of Sulphates and Salts of Barium.*

By William Robert Lang and Thos. Boles Allen.

N. Tarugi and G. Bianchi (*Gazzetta*, 1906, **36**, i, 347) describe an apparatus for the rapid and exact estimation of sulphates and salts of barium by a volumetric method based on the rapid clearing of turbid solutions in narrow tubes. (For a short description of their apparatus



see Abstr., 1906, **90**, ii, 627.) The authors have modified this apparatus materially; the following short description and diagram will serve to explain it.

The vessel, *A*, containing the acidified sulphate is placed on a flat burner, the approximate amount of barium chloride solution, ascertained by previous rough experiments, run directly into the flask, the stopper, *O*, with its attachments, inserted, and the contents kept at the boiling point. *FF* is a T-tube, on the branch, *G*, of which is fixed a small piece of rubber tubing with a pinchcock, at this stage of the experiment left open to the air. *N* is a small thistle-shaped tube filled with glass-wool which is found materially to clear the turbid solution as it passes up to the narrow tube. The pinchcock, *H*, is then

closed and a slight pressure on *M* forces a portion of the contents of the flask through *N* and up *B* until the portion *C* is filled, when the stopcock, *E*, is closed. The whole pressure on the flask can then be relieved by opening the pinchcock, *H*. The liquid in *C* clears very rapidly and the standard barium chloride solution may be added. If this produces a turbidity, *E* is opened and the solution washed down into the flask ; a very complete mixing is then obtained by alternately compressing *M*, with *G* open to the air, placing the finger on the orifice of the short rubber tube, *K*, and releasing *M*, thus causing air to be drawn through *N* and to bubble through the solution.

The process of forcing the liquid up the tube, titrating, washing it down again, and mixing is repeated until a further addition of barium chloride solution causes no turbidity. The mean between the number of c.c. used up to the point of having an evident turbidity and the quantity necessary to the point where none is perceptible is taken as the amount of barium chloride solution consumed in the precipitation of the sulphate. As the amounts of barium salt and sulphate in solution approximate to each other, so the rapidity of the clearing increases, and when the reaction has almost reached the end-point this clarification is very nearly instantaneous.

Experiments were undertaken in this apparatus with the solutions of sulphates and barium salts given in the following tables :

TABLE I.

Using 0·0958*N*– H_2SO_4, 1 c.c. = 0·0046 gram (SO_4).
„ 0·1101 *N*– $Ba(NO_3)_2$, 1 „ = 0·00485 „ (SO_4).

No. of c.c. of H_2SO_4 taken.	Equal to gram (SO_4).	No. of c.c. of $Ba(NO_3)_2$ taken.	Equal to gram (SO_4).	Error in per cent.
10·42	0·0479	10·00	0·0485	−1·0
10·60	0·0488	10·00	0·0485	+0·6
10·52	0·0484	10·00	0·0485	−0·2
10·58	0·0487	10·00	0·0485	+0·4
16·80	0·0773	16·00	0·0776	−0·3
15·71	0·0722	15·00	0·0727	−0·7

Average error −0·55 and +0·5, giving a mean error of 0·025 per cent.

TABLE II.

Using 0·9981 *N*– H_2SO_4, 1 c.c. = 0·0479 gram (SO_4).
„ 0·1101 *N*– $Ba(NO_3)_2$, 1 „ = 0·00485 „ (SO_4).

No. of c.c. of H_2SO_4 taken.	Equal to gram (SO_4).	No. of c.c. of $Ba(NO_3)_2$ taken.	Equal to gram (SO_4).	Error in per cent.
5·05	0·2419	50·00	0·2425	0·4
5·08	0·2433	50·00	0·2425	0·4
5·09	0·2438	50·00	0·2428	0·5
			Average error.....	0·43

TABLE III.

Using 0·2039 N – H_2SO_4, 1 c.c. = 0·0099 gram (SO_4).
„ 0·1101 N – $Ba(NO_3)_2$, 1 „ = 0·00485 „ (SO_4).

No. of c.c. of H_2SO_4 taken.	Equal to gram (SO_4).	No. of c.c. of $Ba(NO_3)_2$ taken.	Equal to gram (SO_4).	Error in per cent.
14·75	0·1460	29·95	0·1453	1·0
14·81	0·1466	30·00	0·1455	0·9
17·35	0·1717	34·90	0·1700	0·6
9·90	0·0980	20·10	0·0975	0·5
			Average error.....	0·75

Solutions of coloured sulphates, such as those of copper and nickel, were also tried, the error in these cases ranging from 0·1 to 0·8 per cent. of the theoretical.

From a study of these results it appears that a single titration will come within 1 per cent. of the value found by gravimetric estimation, and, if a sufficient number of titrations are made, the results can be obtained to within 0·5 per cent. of the gravimetric value (compare Table I.). It may be added that the presence of free acid materially aids the precipitation, greatly increasing the rate of precipitation of the turbid liquid in the narrow tube.

The determination of sulphur in iron pyrites by this method gave :

	Gravimetric.	*Volumetric.*
Iron salts present.....	52·13 per cent.	52·20 per cent.
Iron salts absent	52·24 „	52·09 „

It would seem that this method might be used in cases where speed is of more importance than absolute accuracy. It has this great advantage, that an estimation agreeing within 0·5 per cent. of the best gravimetric method can be made in from three-quarters to one hour ; that is, by taking the mean of four or five volumetric readings.

The Determination of Sucrose by Fehling's Solution.

Experiments with this apparatus were made to determine the best conditions under which the above could be most accurately carried out.

TABLE IV.

	No. of c.c. of sucrose taken.	Equal to gram sucrose.	Dilution in c.c.	Time of heating in minutes.	No. of c.c. of solution used.	Equal to gram sucrose.	Error in per cent.
(1)	10·00	0·2278	200	5	45·50	0·2275	0·2
(2)	10·00	0·2278	150	5	45·65	0·2283	0·3
(3)	5·00	0·1136	100	5	22·75	0·1138	0·2
(4)	10·00	0·2278	150	5	45·64	0·2282	0·2
(5)	10·01	0·2280	150	5	45·58	0·2279	0·1
(6)	10·00	0·2278	175	5	45·62	0·2281	0·1
(7)	10·00	0·2278	150	8	45·65	0·2283	0·3
(8)	2·00	0·0456	200	5	9·02	0·0451	1·0
(9)	5·00	0·1136	450	5	22·90	0·1145	1·0
(10)	10·00	0·2278	450	5	45·92	0·2296	0·9
(11)	10·00	0·2278	150	15	45·82	0·2292	1·0
(12)	5·00	0·1136	100	20	23·20	0·1160	2·0

These results are some of a number of determinations, and they show that, if suitable conditions are obtained, the results give excellent agreement with the theoretical. The conditions are, first, that the Fehling's solution should be added to the boiling liquid to within 1 c.c. of the correct amount, this being obtained by previous rough titrations; secondly, that the strength of the sucrose in the flask should not be more than 0·15 gram in from 75—100 c.c. of water, and thirdly, that the time of heating should not be more than from five to eight minutes.

CHEMICAL LABORATORY,
UNIVERSITY OF TORONTO.

R. CLAY AND SONS, LTD., BREAD ST. HILL, E.C., AND BUNGAY, SUFFOLK.

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A Benzene Model on One Plane for Lecture Purposes.

W. R. Lang.

[Reprinted from the Journal of the American Chemical Society
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A Benzene Model, on One Plane, for Lecture Purposes.—This model is intended as an aid to teachers in explaining the theory of the constitution of benzene. Any theory regarding its constitution must account for and explain the behavior of benzene towards reagents and its power of forming derivatives. In the aliphatic series it is usual to represent the hydrocarbons graphically with the carbon and hydrogen atoms arranged as in an open chain. The model held as in Fig. 1 would thus represent benzene, showing eight unsatisfied affinities.

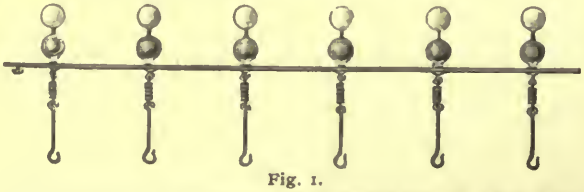

Fig. 1.

But the following summarized characteristics of this body cannot be reconciled with such an open-chain representation, namely :

(*a*) That each of its hydrogen atoms bears the same relation to the molecule, as is evident by the non-existence of isomeric mono-substitution compounds.

(*b*) The formation of benzene as a constant product of the decomposition of the other members of the aromatic series.

(*c*) The formation of hexa-additive compounds (and no more) and the ready breaking up of these into a tri-substitution product.

(*d*) The formation of three di-substitution products.

(*e*) The evident "saturated" nature of benzene.

It is clear from (*c*) that there can be only six unsatisfied affinities, so, if the model is bent round to form a circle, as in Fig. 2, thus linking the first carbon atom to the last, the number of unsatisfied affinities is shown as being reduced to six, and, in addition, each carbon and hydrogen atom is represented as bearing the same relation to the molecule, all being similarly linked.

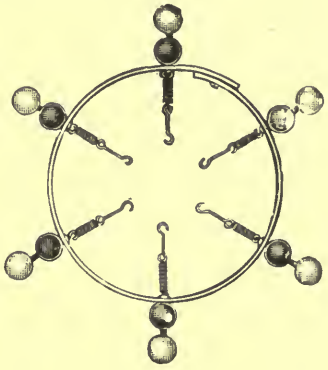

FIG. 2

But the fourth valence of the carbon atoms still appears as unoccupied; these may be represented as acting *towards* the centre—as in the Armstrong-Baeyer formula, or the diagonally opposite atoms may be linked together (Claus); figure 3. If this is done, the model will then represent an exceedingly stable molecule.

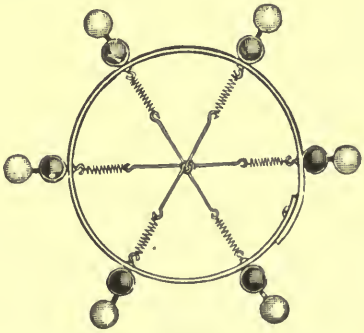

FIG. 3

Small spiral springs are used in the interior of the "ring," to permit of the rapid and secure fastening together of the diagonally opposite

linkings in the last position. The model can readily be constructed from a flexible brass band 1–2 cms. wide, with stiff wires soldered through holes in the rim, while corks of different colors serve admirably for the carbon and hydrogen atoms. It is, however, obtainable from Messrs. Baird and Tatlock, London, E. C.

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Sur la dissociation du chlorure de cadmium hexammoniacal;

PAR MM. W.-R. LANG ET A. RIGAUT.

« Isambert (¹) a montré que l'on peut caractériser les composés chimiques définis, dissociables dans un système hétérogène, par la constance de leurs tensions de dissociation. L'étude qu'il a faite des combinaisons de l'ammoniaque avec les sels est restée classique.

» Nous avons étudié, à ce point de vue, les combinaisons de l'ammoniaque avec le chlorure de cadmium, en employant l'ammoniaque à l'état gazeux, liquéfié ou dissous.

» A la température ordinaire, par un courant prolongé de gaz ammoniac sur le chlorure de cadmium anhydre, il y a fixation de 6 molécules de AzH^3 avec gonflement de la masse (²). Nous avons préféré faire réagir l'ammoniac liquéfié sur le chlorure de cadmium fondu et concassé.

» Le gaz ammoniac sec est dirigé sur un poids connu de sel, refroidi à — 80° jusqu'à ce qu'il y ait un notable excès d'ammoniac liquide, baignant la masse blanche et gonflée qui s'est formée.

» Le tube scellé à la lampe est abandonné pendant dix-huit heures; au bout de ce temps, on ouvre le tube préalablement refroidi à — 80°, et on le réchauffe jusqu'à — 30° par addition de chlorure de méthyle. L'ammoniac liquide s'évapore. Dans certaines de nos expériences, on a laissé réchauffer jusqu'à 0°, après quoi on ferme le tube à la lampe. L'augmentation de poids correspond à la formule $CdCl^2 6AzH^3$.

» En présence d'un excès d'ammoniac liquide, et au bout de plusieurs jours, le produit, d'abord amorphe, devient nettement cristallin.

» Chauffé à 100°, le chlorure hexammoniacal perd 4 molécules d'AzH^3 et se trans-

(¹) ISAMBERT, *Annales de l'École Normale*, 1868.

(²) CRAFT, *Philosophical Mag.*, vol. XXI, 3ᵉ série, p. 355.

forme en chlorure diammoniacal inodore qui, comme le composé correspondant de zinc, ne commence à se décomposer que vers 210°, et à 360° la décomposition n'est pas encore complète.

» Dans cette décomposition du chlorure diammoniacal jusqu'à 400°, température de fusion du $CdCl^2$, il ne se produit qu'une trace d'oxychlorure et de chlorhydrate d'ammoniaque.

» Pour déterminer les tensions de dissociation du chlorure de cadmium hexammoniacal, nous avons employé la disposition de M. Jarry (1) qui permet d'éviter le contact des graisses des robinets avec le gaz ammoniac :

T.	P.	T.	P.
°C.	cm	°C.	cm
0	4,6	50	45,5
13	6,8	52	51,1
22	13,5	59	63,1
25	15,2	60	69,6
31	18,1	61	71,1
39	23,5	63	77,6
44	29,0	65	83,1
48	41,1	69	93,1

» On voit que, au delà de 62°, le composé $CdCl^2 6AzH^3$ ne peut exister. Comme, d'autre part, à 100°, c'est le composé $CdCl^2 2AzH^3$ qui est stable, ce sera entre 62° et 100° qu'il faudra préparer les composés intermédiaires.

» Par voie humide, on obtient très facilement le composé diammoniacal anhydre. En arrosant le chlorure de cadmium hydraté avec la solution ammoniacale à 20 pour 100, de façon à la mouiller complètement, on a une combinaison avec dégagement de chaleur, augmentation de volume. Les cristaux deviennent opaques; séchés à froid sur la chaux ou à l'étuve à 100°, ils répondent à la formule $CdCl^2, 2AzH^3$. C'est encore le même produit qu'on obtient en évaporant la solution de chlorure de cadmium dans l'ammoniaque sur la chaux, ou en recueillant le précipité qui se forme lorsqu'on chauffe à 50° la même solution.

» Pour obtenir un produit contenant plus de 2 molécules de AzH^3 avec la solution ammoniacale, il faut faire passer un courant de gaz ammoniac dans une solution claire de chlorure de cadmium dans l'ammoniaque à 20 pour 100 maintenue à 0°; il se fait un abondant précipité de petits cristaux transparents qui, séchés au papier et à la presse, deviennent opaques en perdant AzH^3. Ces cristaux avaient été obtenus une fois par M. André (2) qui leur avait donné la formule $CdCl^2, 5AzH^3$. D'après nos ana-

(1) Jarry, *Thèse de la Faculté des Sciences de Paris*, 1899.

(2) *Comptes rendus*, t. CIV, p. 908.

lyses, nous serions conduits à admettre la formule de Craft, $CdCl^2, 6AzH^3$, ce qui confirmerait le fait établi par M. Jarry (1) pour les chlorures d'argent ammoniacaux obtenus avec la dissolution ammoniacale; à savoir que la formation et la décomposition de ces chlorures s'arrêtent quand l'eau est saturée sous une pression égale à leur tension de dissociation.

» Nous avons d'ailleurs déterminé les tensions de dissociation de ce composé. A 22°, nous avons trouvé une tension de $14^{cm},7$ au lieu de $13^{cm},5$. L'excès de tension obtenu avec ce produit tient à la petite quantité d'eau interposée qu'il contenait encore.

» Il nous paraît dès lors possible d'obtenir les mêmes combinaisons ammoniacales, soit avec le gaz ammoniac, soit avec une dissolution convenablement concentrée. »

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(1) Jarry, *Thèse de la Faculté des Sciences de Paris*, 1899.

(31 juillet 1899.)

GAUTHIER-VILLARS, IMPRIMEUR-LIBRAIRE DES COMPTES RENDUS DES SEANCES DE L'ACADÉMIE DES SCIENCES.
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OUTLINE OF QUALITATIVE ANALYSIS

W. R. LANG

SECOND EDITION

TORONTO
THE UNIVERSITY PRESS
1910

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Qualitative Analysis means, in its widest sense, the various processes and operations that the chemist makes use of to determine of what a substance is composed. Practice in this, at the same time, familiarizes the student with the appearance and properties of substances, the word being used in its more limited sense of signifying definite elements or homogeneous chemical compounds. In order to determine of what a substance is composed, characteristic "reactions" are caused to occur between the substance under examination and some known body which is termed a "reagent." For example, when a solution in water of common salt (NaCl) is brought in contact with a solution of nitrate of silver ($AgNO_3$) the chloride of silver (AgCl) is always formed, and this, being insoluble in water, appears in the form of a "precipitate." The reaction may be expressed by the equation $NaCl + AgNO_3 = \mathbf{AgCl} + NaNO_3$. So also, when chloride of barium reacts with a soluble sulphate such as sodium sulphate or hydrogen sulphate (sulphuric acid), insoluble barium sulphate is precipitated:

$$BaCl_2 + Na_2SO_4 = \mathbf{BaSO_4} + 2\ NaCl.$$

It will be seen that the formation of barium sulphate, which has very definite characteristics that distinguish it from all other white precipitates, notably its almost complete insolubility in hot acids, serves to identify the presence of the metal barium in the salt experimented on, and, at the same time, that of a sulphate in the reagent added, or *vice versa*.

In analytical chemistry salts in solution may be considered to consist of a metallic ion and an acid ion: in the case of sodium chloride a solution of this would contain a metallic ion $\overset{+}{Na}$ and an acid ion $\overset{-}{Cl}$. So, also, a solution of ammonium chloride has a "metallic" ion ($\overset{+}{NH_4}$) and an acid ion $\overset{-}{Cl}$. In analysis the object is to make one or other of these ions form some new combination whose properties will be characteristic of that one and that one only. For example, a solution of lead chloride when treated with hydrogen sulphide will yield a black precipitate of lead sulphide:

$$\overset{+}{Pb}\overset{-}{Cl_2} + \overset{+}{H_2}\overset{-}{S} = \mathbf{PbS} + 2\ \overset{+}{H}\overset{-}{Cl}$$

the lead sulphide has definite properties which may be used to distinguish it from all other black sulphides. The same lead chloride solution when treated with silver nitrate yields a precipitate of silver chloride:

$$\overset{+}{Pb}\overset{-}{Cl_2} + 2\ \overset{+}{Ag}\overset{-}{NO_3} = \mathbf{2\ AgCl} + \overset{+}{Pb}\ 2\ \overset{-}{NO_3}$$

this silver chloride has definite properties peculiar to itself and so the experimenter is satisfied that the substance he has contains lead and chlorine, that it is the chloride of lead, in fact.

Analysis of a salt thus means detecting the metallic ion, or metal, and the acid ion. This latter may consist of one element, as in the above example, or of a group of elements as in the salt potassium chlorate: here the ions are $\overset{+}{K}$ and $\overset{-}{ClO_3}$; in this acid ion the chlorine cannot be precipitated and removed as silver chloride, the reaction takes place between the ions thus,

$$\overset{+}{K}\ |\ \overset{-}{ClO_3} + \overset{+}{Ag}\overset{-}{NO_3} = AgClO_3 + KNO_3$$

and silver chlor*ate* is formed which is quite a different substance from the chlor*ide* of that metal.

It is presumed that the student has been through an elementary course of quantative chemistry and is familiar with the properties of acids and alkalies and with the methods of washing precipitates, filtration and general manipulation. What follows is a short guide to enable the student to undertake the identification of simple salts and afterwards of mixtures of several. First are given the reactions for the metals, then those for the acid radicles; then follow analytical tables. *Constant reference will be required from these to the "tables of differences" to select confirmatory tests.* On the page opposite each metal or acid radicle are placed equations intended to explain the individual tests performed. In many cases, it must be remembered, these are only approximations to the actual facts. The insoluble substances, or precipitates, formed in the course of the reactions are printed in **heavy type**, products gaseous at the temperature of the reaction in *italics*. It should be noticed how the corresponding reactions for metals of the same analytical group closely resemble each other. That the reactions take place *in aqueous solution* is, of course, understood.

The systematic grouping of the metals (or bases) depends on their behaviour with certain *group reagents*, as they are called, and the groups are as follows:

GROUP I. (Hydrochloric Acid Group). The metals that are precipitated by dilute hydrochloric acid; that is, whose chlorides are insoluble (or comparatively so) in water. They are Lead, Silver, Mercury (*-ous*).

GROUP II. (Hydrogen Sulphide group). The metals precipitated by hydrogen sulphide in the presence of dilute acids; that is, whose sulphides are insoluble in dilute acids. They are Lead, Mercury (*-ic*), Bismuth, Copper, Cadmium, Arsenic, Antimony, Tin.

GROUP III. *A* (Ammonia group; often called the Iron group). The metals whose hydroxides are precipitated by ammonia in the presence of ammonium chloride and are not dissolved by an excess of ammonia. They are Iron, Aluminium, Chromium.

GROUP III. *B* (Ammonium Sulphide group). The metals whose sulphides are precipitated by ammonium sulphide in the presence of ammonia. They are Zinc, Manganese, Nickel, Cobalt.

NOTE: As a comparison with Group II. the sulphides of Groups III *A* and *B* might be said to be *soluble* in dilute acids, with the exception of those of Nickel and Cobalt.

GROUP IV. (Ammonium Carbonate group or Alkaline-earth group). The metals whose carbonates are precipitated by ammonium carbonate in the presence of ammonium chloride. They are Barium, Strontium, Calcium.

GROUP V. The metals which are not precipitated by any of the above reagents in neutral, acid or alkaline solution. They are Magnesium, Potassium, Sodium, Ammonium (NH_4).

In performing the reactions that follow, and in subsequent analytical work, the student should note what are the common soluble and insoluble salts of each metal and of each acid radicle. This knowledge can only be acquired by *practice and observation*.

FLAME TESTS.

VIOLET—*Potassium.*

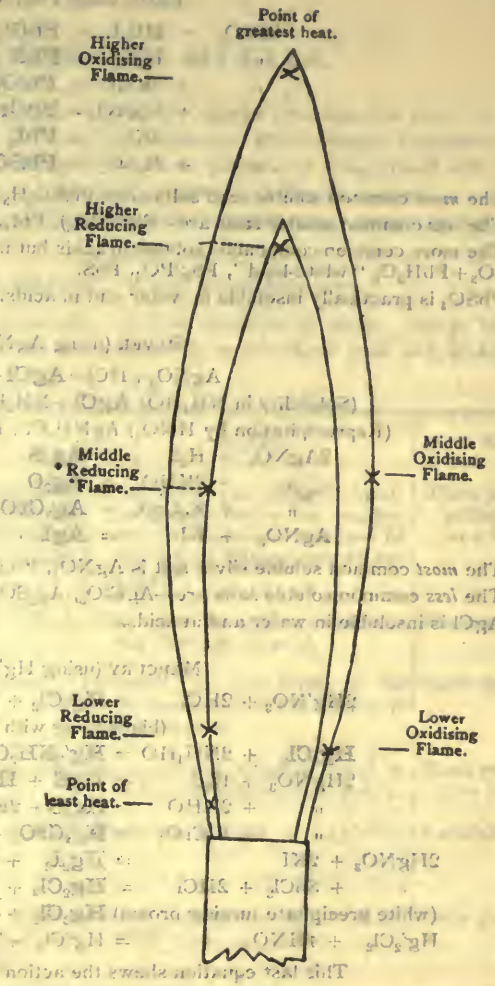
YELLOW—*Sodium.*

YELLOW-GREEN—*Barium.*

YELLOW-RED—*Calcium.*

CRIMSON—*Strontium.*

GREEN—{ *Copper.* / *Boracic Acid.* (*Boric Acid*)



To apply a FLAME TEST, make a small loop at the end of a platinum wire, heat it, and gather up with it some of the salt under examination. Heat the salt in the outer part of the flame, where it will gradually be volatilized, its vapour decomposed and the metal liberated, which will impart to the flame a characteristic colour. These colours are often best obtained by moistening the salt on the wire with a little strong hydrochloric acid.

The sodium flame will be found to be very persistent and may mask that of other metals.

The platinum wire must be kept perfectly clean: this can be done by dipping in hydrochloric acid and heating it several times till no colouration is imparted to the flame.

LEAD (using $Pb2NO_3$).

$$Pb2NO_3 + 2HCl = \mathbf{PbCl_2} + 2HNO_3$$
$$" + H_2S = \mathbf{PbS} + "$$
$$" + 2KHO = \mathbf{Pb(OH)_2} + 2KNO_3$$
$$" + K_2CrO_4 = \mathbf{PbCrO_4} + "$$
$$" + 2KI = \mathbf{PbI_2} + "$$
$$" + H_2SO_4 = \mathbf{PbSO_4} + 2HNO_3$$

The *more* common soluble lead salts are—$Pb2(C_2H_3O_2)$, $Pb2(NO_3)$, $PbCl_2$.

The *less* common soluble salts are—$Pb2(ClO_3)$, PbI_2, $PbBr_2$.

The more common compounds soluble in acids but insoluble in water are—PbO, Pb_3O_4, PbO_2, $2PbCO_3 + PbH_2O_2$ "white-lead", Pb_32PO_4, PbS.

$PbSO_4$ is practically insoluble in water and in acids.

SILVER (using $AgNO_3$).

$$AgNO_3 + HCl = \mathbf{AgCl} + HNO_3$$
(Solubility in NH_4HO) $\mathbf{AgCl} + NH_4HO = AgNH_3Cl + H_2O$
(Reprecipitation by HNO_3) $AgNH_3Cl + HNO_3 = \mathbf{AgCl} + NH_4NO_3$
$$2AgNO_3 + H_2S = \mathbf{Ag_2S} + 2HNO_3$$
$$" + 2KHO = \mathbf{Ag_2O} + 2KNO_3 + H_2O$$
$$" + K_2CrO_4 = \mathbf{Ag_2CrO_4} + 2KNO_3$$
$$AgNO_3 + KI = \mathbf{AgI} + KNO_3$$

The *most* common soluble silver salt is $AgNO_3$, "lunar caustic".

The *less* common soluble salts are—$AgClO_3$, Ag_2SO_4, $AgC_2H_3O_2$.

AgCl is insoluble in water and in acids.

MERCURY (using $Hg'NO_3$).

$$2Hg'NO_3 + 2HCl = \mathbf{Hg_2Cl_2} + 2HNO_3$$
(blackening with NH_4HO)
$$\mathbf{Hg_2Cl_2} + 2NH_4HO = \mathbf{Hg'_2NH_2Cl} + NH_4Cl + 2H_2O$$
$$2HgNO_3 + H_2S = \mathbf{HgS} + \mathbf{Hg} + 2HNO_3$$
$$" + 2KHO = \mathbf{Hg_2O} + 2KNO_3 + H_2O$$
$$" + K_2CrO_4 = \mathbf{Hg_2CrO_4} + 2KNO_3$$
$$2HgNO_3 + 2KI = \mathbf{Hg_2I_2} + 2KNO_3$$
$$" + SnCl_2 + 2HCl = \mathbf{Hg_2Cl_2} + SnCl_4 + 2HNO_3$$
(white precipitate turning brown) $\mathbf{Hg_2Cl_2} + SnCl_2 = \mathbf{Hg_2} + SnCl_4$
$$Hg'_2Cl_2 + 4HNO_3 = Hg''Cl_2 + Hg''2NO_3 + N_2O_4 + 2H_2O$$

This last equation shews the action of HNO_3 on calomel.

The most common soluble salt is Hg_22NO_3 ($HgNO_3$).

Hg_2Cl_2, (HgCl), "calomel", is insoluble in water and in acids.

REACTIONS FOR THE METALS.

NOTE.—In working through this and the following sheets, students should complete the tests for each element before proceeding to the next, *i.e.*, should work from the top to the foot of each column. For example, a solution of lead nitrate should be made by dissolving some of the salt with hot water in a test-tube; small portions of this, diluted with water, are then taken and the respective reagents under "Reagent Employed" added to such portions and the effects noted.

A ——— in Tables of Differences indicates that the test is not used for that element or radicle, not necessarily that nothing happens.

GROUP I.—SILVER GROUP. (Lead, Silver, Mercury).

The chief characteristic of these metals is the insolubility of their chlorides in water. Since, however, lead chloride ($PbCl_2$) is somewhat soluble in water it is never completely precipitated by hydrochloric acid and, in doing an analysis of an unknown salt, is therefore found also in Group II.

Reagent Employed.	Lead.	Silver.	Mercury. (-ous)
Hydrochloric acid (HCl)	White ppt. of $PbCl_2$, sol. in boiling water and crystallizing out on cooling: addition of ammonia to ppt. causes no apparent change.	White curdy ppt. of AgCl, insol. in boiling water but readily sol. in ammonia: addition of nitric acid causes ppt. to reappear.	White ppt. of Hg_2Cl_2, insol. in boiling water but blackened on addition of ammonia.
Ammonium sulphide $(NH_4)_2S$	Black ppt. of PbS, sol. in boiling dilute nitric acid.	Black ppt. of Ag_2S, sol. in boiling dilute nitric acid.	Black ppt.
Ammonia (NH_4HO), very dilute.	White ppt. insol. in excess of reagent.	Probably no ppt. owing to its extreme solubility in excess of the reagent.	Black ppt. insol. in excess.
Potassium hydrate (KOH)	White ppt. slightly sol. in excess.	Brownish ppt. of AgOH, insol. in excess but soluble in ammonia.	Black ppt. insol. in excess and also in ammonia.
Potassium chromate (K_2CrO_4) or potassium bichromate ($K_2Cr_2O_7$)	Bright yellow ppt. sol. in KOH.*	Chocolate red ppt. of Ag_2CrO_4.	Reddish ppt.
Potassium iodide (KI)	Yellow ppt. of PbI_2, sol. in boiling water from which it separates out on cooling.	Pale yellow ppt. of AgI, insol. in nitric acid.	Dark green ppt. of Hg_2I_2.
Sulphuric acid (H_2SO_4) dilute.	White ppt. of $PbSO_4$, sol. in hot hydrochloric acid from which it deposits crystals of $PbCl_2$ on cooling.	———	———

* NOTE.—It must be remembered that only a certain amount of any precipitate can be dissolved by a definite quantity of a reagent. In the case of lead chromate dissolving in potassium hydrate the following reaction expresses what occurs: $PbCrO_4 + 4\,KHO = K_2OPbO + K_2CrO_4 + 2\,H_2O$. Thus, taking the weights of the reacting substances, 224 grams of potassium hydrate can dissolve 333 grams of lead chromate, but no more, and if the amount of precipitate is, in any case whatever, greater than the proportion of the reagent which can dissolve it then some will remain over and the student will imagine that the precipitate is altogether insoluble. In *all cases* when a precipitate has to be dissolved in a reagent the contents of the tube should be boiled to cause the precipitate to become granular and then allowed to settle; the supernatant liquid should be poured off, hot water added, the whole boiled, allowed to settle and the wash-water decanted, three or four times, thus *washing* the precipitate free from any compound that might react with the reagent added for the purpose of dissolving the original precipitate. This process is called "washing by decantation." Of the washed precipitate only a small portion should be taken mixed with a little water for determining its solubility, or the reverse, in such reagent. This applies equally to the second sentence of the preliminary note to this table, with reference to obtaining your solution for the tests that follow, and to making the "original solution" for use with the analytical tables later on. A *small* portion, only, of the salt is put in the solvent and, if it dissolves, more is added till a concentrated solution is obtained.

MERCURY (using $Hg''Cl_2$).

$$Hg''Cl_2 + H_2S = \mathbf{HgS} + 2HCl$$
$$\text{"} + NH_4HO = \mathbf{Hg''NH_2Cl} + HCl + H_2O$$
("white precipitate")
$$\text{"} + 2KHO = \mathbf{HgO} + 2KCl + H_2O$$
$$\text{"} + 2KI = \mathbf{HgI_2} + \text{"} + \text{"}$$
$$2Hg''Cl_2 + SnCl_2 = \mathbf{Hg'_2Cl_2} + SnCl_4$$
$$\mathbf{Hg'_2Cl_2} + SnCl_2 = \mathbf{Hg_2} + SnCl_4$$

The most common soluble mercuric salts are $HgCl_2$ and $Hg2NO_3$; the former is "corrosive sublimate."
$HgBr_2$ and Hg2CN are also soluble, but less commonly met with.
HgO is soluble in acids. HgI_2 is soluble in KI and is used in Medicine.
HgI_2 dissolved in KI yields a compound HgI_22KI, which solution, made alkaline with KHO, constitutes "Nessler's Reagent" for detecting and estimating small quantities of ammonia with which it gives a brown colouration or precipitate, $HgNH_2I$.
$Hg2NO_3$ and $HgSO_4$ are decomposed by the addition of much water yielding insoluble compounds containing an excess of base.

BISMUTH (using $BiCl_3$ dissolved in HCl).

$$2BiCl_3 + 3H_2S = \mathbf{Bi_2S_3} + 6HCl$$
$$\text{"} + 3KHO = \mathbf{Bi(OH)_3} + 3KCl$$
$$\text{"} + 3NH_4HO = \mathbf{Bi(OH)_3} + 3NH_4Cl$$
$$3BiCl_3 + 3H_2O = \mathbf{Bi_2O_3BiCl_3} + 6HCl$$

or, more simply, $BiCl_3 + H_2O = \mathbf{BiOCl} + 2HCl$: this reaction is reversible, the formation of a precipitate or its solution depending on the relative amounts of water, acid, and bismuth salt present.

$BiONO_3$, $Bi3NO_3$ and $BiCl_3$ are the common salts. They are decomposed by water, but may be retained in solution by an excess of acid. The carbonate of bismuth is used in Medicine.

COPPER (using $CuSO_45H_2O$).

$$CuSO_4 + H_2S = \mathbf{CuS} + H_2SO_4$$
$$\text{"} + 2KHO = \mathbf{Cu(OH)_2} + K_2SO_4$$
$$\mathbf{Cu(OH)_2} \text{ boiled with water} = \mathbf{CuO} + H_2O$$
$$2CuSO_4 + K_4Fe6CN = \mathbf{Cu_2Fe6CN} + 2K_2SO_4$$
$$(a)\quad 4CuSO_4 + 6NH_4HO = \mathbf{CuSO_43Cu(OH)_2} + 3(NH_4)_2SO_4$$
$$(b)\quad \mathbf{CuSO_43Cu(OH)_2} + 3(NH_4)_2SO_4 + 10NH_4HO = 4Cu(NH_3)_4SO_4.H_2O + 12H_2O$$

These are explanatory of the blue precipitate formed on adding NH_4HO to a salt of copper and which dissolves to a deep blue liquid on addition of excess of the reagent. *Notice how the action of NH_4HO differs from that of KHO in the case of Copper and of Mercuric salts.*

The more common cupric salts soluble in water are—$CuSO_4$, $CuCl_2$, $Cu2NO_3$.
$Cu2(C_2H_3O_3)$ and $CuBr_2$ are less common.
CuO, $CuCO_3$, $CuHAsO_3$ are soluble in acids.

CADMIUM (using $CdCl_2$).

$$CdCl_2 + H_2S = \mathbf{CdS} + 2HCl$$
$$\text{"} + 2KHO = \mathbf{Cd(OH)_2} + 2KCl$$
$$\text{"} + 2NH_4HO = \mathbf{Cd(OH)_2} + 2NH_4Cl$$

$CdCl_2$, $Cd2NO_3$, $CdSO_4$, $Cd2C_2H_3O_2$ are the more common soluble salts.
$CdBr_2$, CdI_2, are less common.

REACTIONS FOR THE METALS.

GROUP II. A.—COPPER GROUP. (Copper, Mercury, Bismuth, Cadmium).

These metals differ from those of Group I. in having their chlorides soluble in water. Their sulphides are precipitated by hydrogen sulphide *in the presence of dilute hydrochloric acid*, and are *insoluble* in caustic alkalies and alkaline sulphides.

Reagent Employed.	Mercury.	Bismuth.	Copper.	Cadmium.
Hydrogen sulphide (H_2S) in presence of dilute HCl.	When H_2S is added slowly, ppt. is at first white and, then changes through orange and brown to black. Ppt. is insol. in hot HCl or HNO_3.	Black ppt. sol. in hot HNO_3.	Black ppt. sol. in HNO_3.	Yellow ppt. sol. in HNO_3.
Ammonia (NH_4HO)	White ppt. of $HgNH_2Cl$.	White ppt.; boil and allow ppt. to settle, pour off solution and dissolve in *the minimum* of HCl: then add *much* water white ppt.	Greenish blue ppt. sol. in excess to a deep blue solution.	White ppt. of $Cd(OH)_2$, soluble in excess.
Potassium hydrate (KOH)	Yellow ppt.	White ppt. turning yellow on boiling.	Greenish blue ppt. insol. in excess and turning black on boiling.	White ppt. insol. in excess.
Potassium iodide (KI)	Bright red ppt. sol. in excess. This ppt. is sol. in excess of $HgCl_2$ also.			——
Potassium ferrocyanide (K_4Fe6CN)			Chocolate red ppt. decomposed by KOH. (A very delicate reaction).	——
Stannous chloride ($SnCl_2$)	White ppt. of Hg_2Cl_2 darkening on addition of more of the reagent.	——	——	——

ARSENIC^{III} (using As_2O_3[1] dissolved by boiling in water).

$$As_2O_3 + 3H_2O = 2H_3AsO_3 \text{ (arsenious acid).}$$
$$" + 2H_2S = \mathbf{As_2S_3} + 3H_2O$$

Solution must be acid with HCl, otherwise only a yellow colouration is produced.

$$\mathbf{As_2S_3} + 3(NH_4)_2S = 2(NH_4)_3AsS_3 \text{ (thioarsen}\textit{ite}\text{)}$$
(colourless ammonium sulphide)

$$\text{or } As_2S_3 + 3(NH_4)_2S + S_x = 2(NH_4)_3AsS_4 + S_{x-3} \text{ (thioarsen}\textit{ate}\text{)}$$
(yellow ammonium sulphide)

On neutralising the thioarsen*ite* with HCl, $\mathbf{As_2S_3}$ is precipitated.

and " " " thioarsen*ate* " " $\mathbf{As_2S_5}$ " "

$$H_3AsO_3 + CuSO_4 + 2NH_4HO = \mathbf{CuHAsO_3} + (NH_4)_2SO_4 + 2H_2O$$

The presence of NH_4HO here is essential in order to neutralise the free H_2SO_4 which is liberated in the reaction

$$H_3AsO_3 + CuSO_4 = CuHAsO_3 + H_2SO_4$$

and in which the precipitate is soluble.

$$H_3AsO_3 + 3AgNO_3 + 3NH_4HO = \mathbf{Ag_3AsO_3} + 3NH_4NO_3 + 3H_2O$$

The presence of NH_4HO is necessary, as in former case, to neutralise the free HNO_3 liberated in the reaction $H_3AsO_3 + 3AgNO_3 = Ag_3AsO_3 + 3HNO_3$.

As_2O_3 is *sparingly* soluble in H_2O, yielding a slightly acid solution of H_3AsO_3 (arsenious acid). It is readily soluble in solutions of the alkalies or alkaline carbonates forming *arsenites*. It dissolves readily in glycerine, and is also soluble in HCl, giving a solution of $AsCl_3$ which substance on further addition of water is hydrolysed yielding arsenious acid thus :—

$$AsCl_3 + 3H_2O = H_3AsO_3 + 3HCl$$

The more common arsenites are—Na_3AsO_3, K_2HAsO_3, and $(NH_4)_3AsO_3$. $CuHAsO_3$ ("Scheele's green") is soluble in acids.

ARSENIC^{V} (using As_2O_5 dissolved by boiling in water).

$$As_2O_5 + 2H_2O = 2H_3AsO_4 \text{ (arsenic acid)}$$
$$" + 2H_2S = As_2O_3 + 2H_2O + \mathbf{S_2}$$

No precipitation of As_2S_5 as might be expected: the H_2S acts as a reducing agent converting the Arsenic Oxide into Arsenious Oxide, after which As_2S_3 is precipitated according to the second equation under ARSENIC^{III}.

$$H_3AsO_4 + CuSO_4 + 2NH_4HO = \mathbf{CuHAsO_4} + (NH_4)_2SO_4 + 2H_2O$$
$$" + 2AgNO_3 + 3NH_4HO = \mathbf{Ag_3AsO_4} + 3NH_4NO_3 + 3H_2O$$

Compare these with corresponding equations and the remarks thereon above.

$$H_3AsO_4 + MgSO_4 + 3NH_4HO = \mathbf{MgNH_4AsO_4} + (NH_4)_2SO_4 + 3H_2O$$

As_2O_5 is sparingly soluble in H_2O, giving an acid solution of H_3AsO_4. It is also soluble in alkalies and alkaline carbonates yielding *arseniates* or *arsenates*. The more common are—Na_2HAsO_4, K_2HAsO_4, and $(NH_4)_2HAsO_4$.

ANTIMONY (using $SbCl_3$ dissolved in dilute HCl).

$$2SbCl_3 + 3H_2S = \mathbf{Sb_2S_3} + 6HCl$$
$$3SbCl_3 + 3H_2O = \mathbf{Sb_2O_3SbCl_3} + 6HCl$$
or, more simply, $SbCl_3 + H_2O = \mathbf{SbOCl} + 2HCl$ (see remarks under Bismuth equations).
$$2SbCl_3 + 6KHO = \mathbf{Sb_2O_3} + 6KCl + 3H_2O$$
$$\mathbf{Sb_2S_3} + 3(NH_4)_2S = 2(NH_4)_3SbS_3$$

If the reactions are done with "tartar-emetic" $K(SbO)C_4H_4O_6$ then no precipitate will be produced with water as above. The presence of $H_2C_4H_4O_6$ or a tartrate prevents antimony salts from yielding precipitates with water.

$$\left\{\begin{array}{l} K(SbO)C_4H_4O_6 + HCl = \mathbf{SbOCl} + KHC_4H_4O_6 \\ \mathbf{SbOCl} + 2HCl = SbCl_3 + H_2O \end{array}\right.$$
$$2K(SbO)C_4H_4O_6 + 3H_2S = \mathbf{Sb_2S_3} + 2KHC_4H_4O_6 + 2H_2O$$

The most common compounds are—$K(SbO)C_4H_4O_6$ (tartar emetic) and $SbCl_3$.

TIN^{II} and ^{IV} (using $SnCl_2$ and $SnCl_4$).

$$SnCl_2 + H_2S = \mathbf{SnS} + 2HCl$$
$$SnCl_4 + 2H_2S = \mathbf{SnS_2} + 4HCl$$
$$SnCl_2 + 2KHO = \mathbf{Sn(OH)_2} + 2KCl$$
$$SnCl_4 + 4KHO = \mathbf{Sn(OH)_4} + 4KCl$$
These hydrated oxides dissolve in excess of KHO yielding stannites and stannates respectively.
$$SnCl_2 + 2HgCl_2 = \mathbf{Hg_2Cl_2} + SnCl_4$$

SnS, SnS_2 dissolve in ammonium sulphide yielding $(NH_4)_2SnS_3$ and $(NH_4)_2SnS_3$ respectively.

Stannous salts: $SnCl_2$ is the most common compound.

Stannic salts: The only common compound is $SnCl_4$.

(1) As_4O_6 more correctly represents the molecule of this oxide but the formula As_2O_3 will be retained here.

REACTIONS FOR THE METALS.

GROUP II. B.—ARSENIC GROUP. (Arsenic, Antimony, Tin).

The sulphides of these metals are precipitated best in an acid solution, and differ from those of the copper group by being soluble alkalies and alkaline sulphides.

NOTE.—Each metal in this group forms two series of compounds which resemble each other in many reactions but also present certain differences. The two classes are distinguished by the terminations *-ic* and *-ous*.

Reagent Employed.	Arsenic (*-ous*).	Arsenic (*-ic*).	Antimony.	Tin (*Stannous*).	Tin (*Stannic*).
H_2S and a few drops of HCl.	Yellow ppt. of As_2S_3 sol. in NH_4HO and in $(NH_4)_2S$; also in HNO_3. Repptd. by HCl.	Yellow ppt. of As_2S_5 on boiling with repeated additions of H_2S.	Orange ppt. sol. in NH_4HO and $(NH_4)_2S$; also in KHO. Repptd. by HCl.	Brown ppt. of SnS sol. in NH_4HO and $(NH_4)_2S$; also in KHO. Repptd. by HCl.	Yellow ppt. of SnS_2 sol. in NH_4HO and $(NH_4)_2S$. Repptd. by HCl.
KHO.	No ppt.	No ppt.	White ppt. of Sb_2O_3 sol. in excess of reagent.	White ppt. of $Sn(OH)_2$ sol. in excess of reagent.	White ppt. sol. in excess of reagent.
$HgCl_2$.	——	——	——	White ppt. of Hg_2Cl_2 becoming darker owing to separation of mercury.	No ppt.
$AgNO_3$ and a few drops of very dilute ammonia.	Light yellow ppt. of Ag_3AsO_3 sol. in excess of NH_4HO and of HNO_3.	Brown ppt. of Ag_3AsO_4 sol. in excess of NH_4HO and of HNO_3.	*Note.*—Addition of water to any compound of Antimony other than the tartrate causes an immediate precipitate, sol. in $H_2\bar{T}$ or in HCl.†	——	——
Ammonio sulphate of copper; (Made by adding NH_4HO to the $CuSO_4$ sol. till blue ppt. at first formed just redissolves).	Green ppt. of $CuHAsO_3$ sol. in NH_4HO and in HNO_3.	Greenish blue ppt. of $CuHAsO_4$ sol. in NH_4HO and in HNO_3.	——	——	——
NH_4Cl, NH_4HO and $MgSO_4$.	No ppt.	White cryst. ppt. of $MgNH_4AsO_4$.	——	——	——
Reinsch's Test. Solution acidified with a few drops of HCl and boiled with a strip of clean copper foil.	Grey stain on the foil. If foil is dried and heated *gently* in a dry test tube a white sublimate of As_2O_3 is formed on the sides of the tube. Dissolve off by boiling with *hot water* and apply the first, fourth and fifth tests in order to confirm.		Foil stained as in the case of arsenic but appearance of stain and behaviour on heating quite different.	——	——
Marsh's Test. Zinc and H_2SO_4 causes evolution of,	Arseniuretted hydrogen (AsH_3).		Antimonetted hydrogen (SbH_3).		

* All compounds of arsenic and of antimony when in contact with a solution evolving hydrogen, yield AsH_3 and SbH_3. The experiment has to be performed in a special apparatus and with great care, and should not be attempted except under the direction of an experienced person.

† The contractions $H_2\bar{T}$ and $H\bar{A}$ are occasionally used to economise space in place of $H_2C_4H_4O_6$ and $HC_2H_3O_2$—tartaric acid and acetic acid respectively. So, also, y in place of 'CN.

Iron, Aluminium, Chromium.

Iron^{II} and ^{III} (using $Fe''SO_4$ and $Fe'''Cl_3$).

$$FeSO_4 + 2NH_4HO = \mathbf{Fe(OH)_2} + (NH_4)_2SO_4$$
$$FeCl_3 + 3NH_4HO = \mathbf{Fe(OH)_3} + 3NH_4Cl$$
$$FeSO_4 + (NH_4)_2S = \mathbf{FeS} + (NH_4)_2SO_4$$
$$2FeCl_3 + 3(NH_4)_2S = \mathbf{2FeS} + \mathbf{S} + 6NH_4Cl$$
$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + \mathbf{S}$$
$$FeSO_4 + K_4Fe6CN = \mathbf{K_2Fe(Fe6CN)} + K_2SO_4$$
$$4FeCl_3 + 3K_4Fe6CN = \mathbf{Fe_4(Fe6CN)_3} + 12KCl$$
("Prussian Blue")
$$3FeSO_4 + 2K_3Fe6CN = \mathbf{Fe_3(Fe6CN)_2} + 3K_2SO_4$$
$$FeCl_3 + 3KCNS = Fe3CNS + 6KCl$$

The more common soluble ferrous salts are—$FeSO_4$, $FeCl_2$, $Fe2NO_3$, and the double sulphate $Fe(NH_4)_22SO_46H_2O$, "Mohr's salt."

The less common soluble salts are—FeI_2, $FeBr_2$, $Fe2(C_2H_3O_2)$.

$FeCO_3$, FeS, and Fe_32PO_4 are soluble in acids.

The more common soluble ferric salts are—$FeCl_3$, Fe_23SO_4, and "iron alum," $KFe2SO_412H_2O$.

The less common soluble compounds are—FeI_3, $FeBr_3$, $Fe3C_2H_3O_2$.

Fe_2O_3 and $FePO_4$ are soluble in acids.

Aluminium (using $KA12SO_4$ or Al_23SO_4).

$$2KAl2SO_4 + 6NH_4HO = \mathbf{2Al(OH)_3} + 3(NH_4)_2SO_4 + K_2SO_4$$

(*a*) $$Al_23SO_4 + 6KHO = \mathbf{2Al(OH)_3} + 3K_2SO_4$$

(*b*) $$\mathbf{Al(OH)_3} + KHO = KAlO_2 + 2H_2O$$

(*c*) $$KAlO_2 + NH_4Cl + 2H_2O = KCl + NH_4HO + \mathbf{Al(OH)_3}$$

$$Al_23SO_4 + 3(NH_4)_2S + 6H_2O = \mathbf{2Al(OH)_3} + 3(NH_4)_2SO_4 + 3H_2S$$

Notice that $(NH_4)_2S$ precipitates the *hydrate*, not the *sulphide*. *Cf.* Chromium.

The more common soluble salts of aluminium are—Al_23SO_4, $AlCl_3$, $KAl2SO_4$, $NaAl2SO_4$, $(NH_4)Al2SO_4$, ("alums").

The less common soluble compounds are—$AlBr_3$, $Al3C_2H_3O_2$.

Chromium (using $KCr2SO_4$ or Cr_23SO_4).

The reactions and equations are similar to those given for Aluminium.

The more common soluble salts are—Cr_23SO_3, $CrCl_3$, $KCr2SO_4$ $12H_2O$ ("Chrome alum").

Also the salts of chromic acid, potassium chromate K_2CrO_4 and potassium bichromate $K_2Cr_2O_7$.

Cr_2O_3—the sesquioxide, is *basic* and forms salts of chromium with acids.

CrO_3—chromic anhydride, is *acid* and forms chromates with bases.

The conversion of salts of chromium into chromates and bichromates and the reverse is best seen from the following equations. It should be noted that *all chromium compounds fused in the presence of air with oxidising agents and carbonates or hydrates of the alkalies yield chromates:* thus—$Cr_2O_3 + 2K_2CO_3$ yields $2K_2CrO_4$.

The addition of dilute acids to K_2CrO_4 converts it into $K_2Cr_2O_7$ (*i.e.*, $K_2CrO_4CrO_3$)—

$$2K_2CrO_4 + H_2SO_4 = K_2Cr_2O_7 + K_2SO_4 + H_2O$$

This $K_2Cr_2O_7$ on treatment with an alkali becomes K_2CrO_4—

$$K_2Cr_2O_7 + 2KHO = 2K_2CrO_4 + H_2O$$

These chromates or bichromates (which are yellow or orange in colour) are converted by reducing agents in the presence of free acid into salts of chromium (violet)—

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S = K_2SO_4 + Cr_23SO_4 + 7H_2O + \mathbf{S_3}$$

and $$K_2Cr_2O_7 + H_2O + 3SO_2 = K_2SO_4 + Cr_23SO_4 + H_2SO_4 + \mathbf{S}$$

REACTIONS FOR THE METALS.

GROUP III. A.—IRON GROUP. (Iron, Aluminium, Chromium).

The sulphides of these metals are soluble in dilute hydrochloric acid and are therefore not precipitated by hydrogen sulphide unless the solution be alkaline. The characteristic group-reagents are ammonia and sulphide of ammonium. The hydrated oxides of these metals precipitated by ammonia are insoluble in excess of the reagent.

NOTE.—Two classes of iron compound are known, which differ in appearance and properties and behave differently with reagents: they are distinguished as *ferrous* and *ferric* compounds respectively and by the symbols (Fe'') and (Fe'''), the dashes indicating the number of chlorine atoms, or their equivalent, which are combined with one atom of iron in the compound. Thus, there are two chlorides of iron which may be represented by the formulae $Fe''Cl_2$ and $Fe'''Cl_3$ (often written Fe'''_2Cl_6). The ferrous compounds are readily converted into ferric compounds by boiling with a little strong nitric acid, or with hydrochloric acid and a crystal of potassium chlorate, and the ferric reduced to ferrous by hydrogen sulphide or other reducing agent.

REAGENT EMPLOYED.	IRON (Fe'').	IRON (Fe''').	ALUMINIUM.	CHROMIUM.	CHROMIUM, (as *chromates*).
Hydrogen sulphide (H_2S) in acid sol.	No ppt.	No ppt.	No ppt.	No ppt.	Colour changes to green and sulphur is pptd., soln. will now give reactions for chromium.
Ammonium sulphide $(NH_4)_2S$	Black ppt. of FeS, sol. in HCl.	Black ppt. of FeS (mixed with sulphur), sol. in HCl.	White ppt. of $Al(OH)_3$, sol. in HCl.	Bluish green ppt. of $Cr(OH)_3$, sol. in HCl.	
Ammonia (NH_4HO)	Dirty green ppt. of $Fe(OH)_2$, turning brown on standing.	Reddish brown ppt. of $Fe(OH)_3$ sol. in acids.	White ppt. of $Al(OH)_3$, best seen on boiling the liquid. Ppt. is sol. in HCl.	Bluish green ppt. of $Cr(OH)_3$; reacts similarly to aluminium ppt.	
Potassium hydrate (KHO).	Same as with NH_4HO.	Same as with NH_4HO.	White ppt. sol. in excess of KHO. Reppted. on addition of NH_4Cl.	Pale green ppt. sol. in excess of KHO. Reppted. on boiling or on adding NH_4Cl.	
Potassium ferrocyanide K_4FeCy_6.	Light blue ppt.	Dark blue ppt. of "Prussian Blue," insol. in HCl but turned brown by KHO.	——	——	
Potassium ferricyanide K_3FeCy_6.	Dark blue ppt. of "Turnbull's Blue."	Soln. darkens but no ppt. is produced.	——	——	
Potassium sulphocyanate (KCNS).	No colouration if solution is free from ferric salt.	Blood red colouration: stable in presence of HCl but destroyed if excess of $HgCl_2$ is added.	——	——	
Fusion with Na_2CO_3 and KNO_3 on foil.	On cooling, brown particles of Fe_2O_3 remain.	Same as with ferrous salts.	——	Yellow mass now containing the *chromate*: this gives a yellow ppt. if dissolved in water and $H\bar{A}$ and $Pb\bar{A}_2$ added.	

Zinc, Nickel, Cobalt, Manganese.

The equations for the reactions of these metals may be put in general terms. Let M = Zn, Mn, Ni or Co.

$$MCl_2 + (NH_4)_2S = \mathbf{MS} + 2NH_4Cl$$

To the solution is usually added NH_4Cl and NH_4HO previous to the addition of $(NH_4)_2S$. These sulphides have varying degrees of solubility in HCl.

$$MCl_2 + 2KHO = \mathbf{M(OH)_2} + 2KCl$$

$$2MCl_2 + K_4Fe6CN = \mathbf{M_2Fe6CN} + 4KCl$$

Special reaction for Zinc, showing solubility of $Zn(OH)_2$ in KHO and reprecipitation by H_2S.

$$\begin{cases} (a)\ ZnCl_2 + 2\ KHO = \mathbf{Zn(OH)_2} + 2KCl \\ (b)\ \mathbf{Zn(OH)_2} + 2\ KHO = K_2ZnO_2 + 2H_2O \\ (c)\ K_2ZnO_2 + H_2S = \mathbf{ZnS} + 2KHO \end{cases}$$

The *more* common soluble zinc salts are—$ZnSO_4$, $ZnCl_2$, $Zn2C_2H_3O_2$.

The *less* common soluble salts are—ZnI_2, $ZnBr_2$, $Zn2ClO_3$, $Zn2NO_3$.

The *more* common zinc compounds insoluble in H_2O but soluble in acids are—ZnO, $ZnCO_3$, ZnS, and a basic carbonate that is used in Medicine.

The *more* common soluble nickel salts are—$NiSO_4$, $NiCl_2$, $Ni2NO_3$.

The *less* common soluble salts are—$NiBr_2$, $Ni2ClO_3$, $Ni2C_2H_3O_2$.

The more common soluble cobalt salts are—$CoSO_4$, $CoCl_2$, $Co2NO_3$.

The less common soluble salts are $CoBr_2$, $Co2ClO_3$, CoI_2, $Co2C_2H_3O_2$.

CoO and Co_2O_3 are soluble in acids.

The common soluble manganese salts are—$MnCl_2$, $MnSO_4$, $Mn2NO_3$. ***The most important of all is potassium permanganate***, $KMnO_4$.

The *less* common soluble salts are—$MnBr_2$, $Mn2C_2H_3O_2$.

$MnCO_3$ and MnO_2 are soluble in acids.

The three most common compounds of manganese are MnO_2, $MnSO_4$ and $KMnO_4$. Like chromium, ***manganese compounds are readily converted into manganates by fusion with alkalies***—

$$MnO_2 + 2KHO + \text{air} = K_2MnO_4 + H_2O \text{ (steam evolved)}$$

This potassium manganate readily becomes potassium *per*manganate by oxidation in aqueous solution—

$$2K_2MnO_4 + \text{oxygen} + \text{water} = \underset{(i.e.,\ 2KMnO_4)}{K_2Mn_2O_8} + 2KHO$$

Manganates and permanganates are converted by reducing agents, in the presence of acids, to ***salts of manganese***—

$$2KMnO_4 + 3H_2SO_4 + 5H_2S = K_2SO_4 + 2MnSO_4 + 8H_2O + \mathbf{S_5}$$

REACTIONS FOR THE METALS.

GROUP III. B.—ZINC GROUP. (Zinc, Manganese, Nickel and Cobalt).

The sulphides of these metals are precipitated from their neutral or alkaline solutions by ammonium sulphide and from their alkaline solutions by hydrogen sulphide. The precipitation of the hydroxides of zinc and manganese by ammonia in Group III. a. is prevented by the presence of ammonium chloride, which forms double salts, $ZnCl_2 2NH_4Cl$ and $MnCl_2 2NH_4Cl$, that are soluble in water, though manganese is precipitated by oxidation if its solution in ammonium chloride and ammonia is exposed to the air. The hydroxides of nickel and cobalt are soluble in excess of ammonia and hence also are kept out of the former group.

Reagent Employed.	Zinc.*	Manganese.*	Nickel.	Cobalt.
Soln. made alkaline with NH_4Cl and NH_4HO, and *a little* $(NH_4)_2S$ added.	White ppt. sol. in dilute HCl, insol. in HA.	Pink ppt. sol. in dilute HCl and in HA.	Black ppt. sol. in hot yellow $(NH_4)_2S$ to a dark soln. Insol. in cold dil. HCl.	Black ppt. insol. in hot yellow $(NH_4)_2S$. Insol. in cold dilute HCl.
Potassium hydrate.	White ppt. sol. in excess of KHO; repptd. by H_2S.	White ppt. turning brown in the air. Insol. in excess.	Green ppt. insol. in excess.	Blue ppt. insol. in excess.
Ammonium hydrate.	No ppt. in presence of NH_4Cl.	White ppt. prevented by presence of NH_4Cl.	Bluish green ppt. of $Ni(OH)_2$ sol. in excess to a violet liquid.	Bluish green ppt. of $Co(OH)_2$ sol. in excess†.
Potassium cyanide (KCN)	———	Brown ppt. sol. in excess.	Yellowish green ppt. of Ni2CN sol. in excess* Reppt. by HCl.	Reddish brown ppt. of Co2CN sol. in excess†.
			†This soln. ppts. $Ni(OH)_3$ on warming with KHO and bromine water.	†This soln. yields *no* ppt. with KHO and bromine water.
Dilute HNO_3 and Pb_3O_4 (red lead).	———	Pink colour produced on warming with a small portion of the manganese salt.		
Fusion on charcoal of solid salt and solid Na_2CO_3.	Incrustation obtained which is *yellow* when hot and *white* when cold.	Fusion with Na_2CO_3 and a little KNO_3 on porcelain lid yields a *green mass*.	———	———

Note.—The manganese present in such a salt as $KMnO_4$ does not give the above reactions. Previous reduction to a salt of manganese must take place. This will occur during the application of the analytical table given on pp. 28, 29. (See last equation on opposite page).

*ZnS and MnS are soluble in dilute mineral acids, consequently H_2S cannot completely precipitate these sulphides from salts of such acids on account of the free acid liberated in the reaction $\frac{ZnCl_2}{MnCl_2} + H_2S = \frac{ZnS}{MnS} + 2HCl$. The sulphides of nickel and cobalt are not soluble in dilute acids.

Alkaline-Earths; Barium, Strontium, Calcium.

Let Æ represent Ba, Sr or Ca.

$$Æ Cl_2 + (NH_4)_2CO_3 = \mathbf{ÆCO_3} + 2NH_4Cl$$
$$\text{"} + Na_2HPO_4 = \mathbf{ÆHPO_4} + 2NaCl$$
$$\text{or } 3ÆCl_2 + 2Na_2HPO_4 = \mathbf{Æ_32PO_4} + 4NaCl + 2HCl$$
$$ÆCl_2 + Na_2SO_4 = \mathbf{ÆSO_4} + 2NaCl$$
$$\text{"} + (NH_4)_2C_2O_4 = \mathbf{ÆC_2O_4} + 2NH_4Cl$$

Special equations for Barium

$$BaCl_2 + CaSO_4 = \mathbf{BaSO_4} + CaCl_2$$
$$\text{"} + K_2CrO_4 = \mathbf{BaCrO_4} + 2KCl$$

The more common soluble Barium salts are—$Ba2NO_3$ and $BaCl_2$.

The less common soluble compounds are—$Ba(OH)_2$, $Ba2ClO_3$, $Ba2C_2H_3O_2$, $BaBr_2$, BaS_2O_3, BaS.

The more common salts of Barium soluble in acids but insoluble in water are—$BaCO_3$, Ba_32PO_4.

The more common soluble Strontium salts are—$Sr2NO_3$ and $SrCl_2$.

The less common soluble compounds are—$Sr(OH)_2$, $Sr2ClO_3$, $Sr2C_2H_3O_2$, $SrBr_2$, SrS_2O_3, SrS.

The more common Strontium salts soluble in acids but insoluble in water are—$SrCO_3$, Sr_32PO_4.

$SrSO_4$ is practically insoluble in water and acids.

The more common soluble Calcium salts are—$CaCl_2$, $Ca2NO_3$, $Ca(OH)_2$, $CaSO_4$. The last named gives "permanent hardness" to water.

The less common soluble compounds are—$Ca2ClO_3$, $Ca2C_2H_3O_2$, $CaBr_2$, CaS_2O_3, $CaSO_3$.

The more common salts soluble in acids but insoluble in water are—$CaCO_3$, Ca_32PO_4, CaC_2O_4, $CaC_4H_4O_6$.

Magnesium (using $MgSO_4$).

$$MgSO_4 + 2KHO = \mathbf{Mg(OH)_2} + K_2SO_4$$
$$\text{"} + 2NH_4HO = \mathbf{Mg(OH)_2} + (NH_4)_2SO_4$$
$$\text{"} + (NH_4)_2CO_3 = \mathbf{MgCO_3} + (NH_4)_2SO_4$$
$$MgSO_4 + NH_4HO + Na_2HPO_4 = \mathbf{MgNH_4PO_4} + Na_2SO_4 + H_2O$$

The more common soluble salts are—$MgSO_4$, $MgCl_2$.

The less common soluble compounds are—$MgBr_2$, MgI_2, $Mg2C_2H_3O_2$, $Mg2NO_3$, $MgSO_3$, MgS_2O_3.

The more common salts soluble in acids but insoluble in water are $MgCO_3$, MgO and Mg_32PO_4.

Potassium.

$$KCl + H_2C_4H_4O_6 = \mathbf{KHC_4H_4O_6} + HCl$$
$$2KCl + PtCl_4 = \mathbf{PtCl_42KCl}$$

Nearly all the potassium compounds are soluble in water.

The following are the more common compounds—KHO, K_2CO_3, KCl, KCy, KI, KBr, $KClO_3$, KNO_3, $KHC_4H_4O_6$.

The following are less commonly met with—K_2CrO_4, $K_2Cr_2O_7$, K_2SO_3, $KHSO_3$, K_2SO_4, $KHSO_4$, $K_2S_2O_3$, $KHCO_3$, $K_2C_2O_4$, K_3PO_4, K_2S, KHS, K_3FeCy_6, K_4FeCy_6, KNO_2, KClO, $KC_2H_3O_2$, $KC_7H_5O_2$, $K_2C_4H_4O_6$, $K_2C_6H_6O_7$, K_3AsO_3, K_2HAsO_4.

Sodium compounds are usually soluble.

The *more* common are—NaHO, Na_2SO_4, $Na_2S_2O_3$, Na_2CO_3, $NaHCO_3$, $Na_2B_4O_7$, Na_2HPO_4, NaCl, $NaNO_3$.

Less common compounds—Na_2CrO_4, $NaHSO_4$, Na_2SO_3, $NaHSO_3$, $Na_2C_2O_4$, NaCy, NaI, NaBr, Na_2S, NaHS, Na_4FeCy_6, NaClO, $NaClO_3$, $NaNO_2$, $NaC_2H_3O_2$, $NaHC_4H_4O_6$, Na_3AsO_3, Na_2AsO_4, $KNaC_4H_4O_6$ "Rochelle Salts."

Ammonium.

$$NH_4Cl + KHO = KCl + H_2O + \mathit{NH_3}$$

The ammonium compounds are usually soluble in water. The more common are—NH_4HO, $(NH_4)_2CO_3$, $(NH_4)_2SO_4$, $(NH_4)_2C_2O_4$, NH_4Cl, NH_4HS, $(NH_4)_2S$, NH_4NO_3.

The less common salts are—$(NH_4)_2CrO_4$, $(NH_4)_2SO_3$, $(NH_4)_2S_2O_3$, $(NH_4)_2B_4O_7$, NH_4Cy, NH_4I, NH_4Br, $(NH_4)_4FeCy_6$, NH_4NO_2, $(NH_4)C_2H_3O_2$, $(NH_4)C_7H_5O_2$, $(NH_4)_2C_4H_4O_6$, $(NH_4)_3AsO_4$.

Table of Differences.

Bases, IV.
Bases, V.

REACTIONS FOR THE METALS.

GROUP IV.—ALKALINE EARTHS. (Barium, Strontium, Calcium).

The sulphides of these metals are soluble in water. The group-reagent is ammonium carbonate which precipitates them in the presence of ammonium chloride in which the carbonate of magnesium is soluble, yielding a double salt $MgCl_2 2NH_4Cl$.

Reagent Employed.	Barium.	Strontium.	Calcium.
Ammonium carbonate $((NH_4)_2CO_3)$	White ppt. sol. in HCl and in HĀ.	White ppt. sol. in HCl and in HĀ.	White ppt. sol. in HCl and in HĀ.
Sulphuric acid (H_2SO_4).	White ppt. immediately.	White ppt. If soln. is very dilute this ppt. only appears on boiling.	White ppt. not formed in dilute solutions.
Calcium sulphate ($CaSO_4$).	White ppt. appearing at once.	White ppt. on boiling.	No ppt.
Potassium chromate (K_2CrO_4).	Yellow ppt. insol. in HĀ.	Yellow ppt. in strong solutions only. Sol. in HĀ.	No ppt.
Ammonium oxalate $((NH_4)_2C_2O_4)$.	White ppt. sol. in HCl and in HNO_3.	White ppt. sol. in HCl and in HNO_3. Sparingly sol. in HĀ.	White ppt. insol. in HĀ. This ppt. appears in the most dilute solutions.
Flame test (see p. 3).	Green.	Red.	Orange Red.

Note.—When concentrated HCl or HNO_3 is added to strong solution of $BaCl_2$ or $Ba2NO_3$ the salt is precipitated, being insoluble in concentrated acids. Dilution with water at once redissolves the precipitate.

GROUP V.—MAGNESIUM AND THE ALKALIES. (Potassium, Sodium and Ammonium).

Reagent.	Magnesium.	Potassium.	Sodium.	Ammonium.
Warmed with KOH	White ppt.	———	———	NH_3 gas given off, recognisable by smell, action on litmus, and by giving white fumes of NH_4Cl when brought in contact with a glass rod moistened with conc. HCl.
Flame test.	———	Pale lilac flame.	Intense yellow flame.	
NH_4Cl, NH_4OH and Na_2HPO_4	White cryst. ppt. of $MgNH_4PO_4$ sol. in HCl.	———	———	———

ACIDS.

Carbonates (using $CaCO_3$ suspended in water).

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$

$$Ca(OH)_2 \text{ (\textit{lime water})} + CO_2 = CaCO_3 + H_2O$$

HCl added to Na_2CO_3 may produce no effervescence at first owing to the formation of the acid carbonate (or bicarbonate):

$$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3$$

K_2CO_3, $KHCO_3$, Na_2CO_3, $NaHCO_3$, $(NH_4)_2CO_3$, and $(NH_4)HCO_3$ are soluble in water.

The remaining normal carbonates are insoluble in water, but soluble in an excess of carbonic acid, when they become acid carbonates, most of which are soluble, *e.g.*, CaH_22CO_3, in which form calcium salts are found in "hard" waters.

Sulphides (using FeS suspended in water).

$$FeS + 2HCl = FeCl_2 + H_2S$$

$$H_2S + Pb2NO_3 = PbS + 2HNO_3$$

K_2S, Na_2S, $(NH_4)_2S$, KHS, $NaHS$, NH_4HS, $(NH_4)_2S$, BaH_2S_2, SrH_2S_2, CaH_2S_2, MgH_2S_2, are soluble in water. Sulphides are decomposed by strong acids giving off H_2S gas.

Sulphites (using Na_2SO_4).

$$Na_2SO_3 + 2HCl = 2NaCl + H_2O + SO_2$$

$$\text{"} + BaCl_2 = BaSO_3 + 2NaCl$$

$$K_2Cr_2O_7 + H_2O + 6SO_2 = K_2SO_4 + Cr_23SO_4 + H_2SO_4 + S$$

(reduction of orange $K_2Cr_2O_7$ to green Cr_23SO_4 by the action of SO_2)

K_2SO_3, Na_2SO_3, $(NH_4)_2SO_3$, $MgSO_3$, $CaSO_3$, and all the acid sulphites are soluble in water.

Both the soluble and insoluble sulphites are decomposed by strong acids giving off SO_2, which can be recognised by its odour.

Thiosulphates (using $Na_2S_2O_3$).

$$Na_2S_2O_3 + 2HCl = 2NaCl + H_2S_2O_3$$

$$H_2S_2O_3 = H_2O + SO_2 + S$$

$Na_2S_2O_3$, $K_2S_2O_3$, $(NH_4)_2S_2O_3$, CaS_2O_3, SrS_2O_3, and MgS_2O_3 are soluble in water. BaS_2O_3 is slightly soluble in water.

REACTIONS FOR THE ACID-RADICLES.

GROUP I.—CARBONIC, HYDROSULPHURIC, SULPHUROUS AND THIOSULPHURIC.

The common acids do not form such well marked groups as do the metals. In these tables those which most resemble one another in their reactions are placed together. The first group gives off characteristic gases when acted upon by hydrochloric acid.

Reagent Employed.	Carbonic.	Hydrosulphuric.	Sulphurous.	Thiosulphuric.
Hydrochloric Acid.	Effervescence owing to liberation of CO_2 which turns lime water ($Ca(OH)_2$) milky.(1)	Gas evolved with odour of rotten eggs which turns filter paper moistened with $Pb2NO_3$(2) black.	Odour of burning sulphur which turns paper moistened with $K_2Cr_2O_7$ green.	Odour of burning sulphur and a white or yellow ppt. of sulphur.
Barium chloride.	White ppt. sol. in HCl.	No ppt.	White ppt. sol. in HCl.	White ppt. sol. in HCl, but which immediately causes a ppt. of sulphur.
A little of the salt placed on a silver coin and moistened with HCl.	———	Black stain produced.	———	———
Silver nitrate.	———	Black ppt.	White ppt. which on heating deposits metallic silver in the form of a dirty powder.	White ppt. which on heating deposits Ag_2S according to equation. $Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4$

(1) CO_2, being heavier than air, can be poured from the test-tube into another about one-third full of lime-water or baryta-water: on closing the latter tube with the thumb and shaking it a ppt. of the carbonate will be formed.

(2) Either Pb2A or $Pb2NO_3$ may be used; any soluble salt of lead, in fact, and these are the only two common ones.

Borates.

The borates of potassium, sodium, and ammonium are soluble in water. The other borates are soluble in acids.

Sulphates (using K_2SO_4).

$$K_2SO_4 + BaCl_2 = \mathbf{BaSO_4} + 2KCl$$

Sulphates fused with $\mathbf{Na_2CO_3}$ on **charcoal** at blow-pipe are reduced to sulphides: $\mathbf{Na_2SO_4 + 4C} = Na_2S + 4CO$.

All the sulphates are soluble in water except $PbSO_4$, $BaSO_4$, and $SrSO_4$. $CaSO_4$ is slightly soluble.

Ortho-Phosphates and Arseniates (using Na_2HPO_4 and Na_2HASO_4).

$$Na_2HPO_4 + NH_4HO + MgSO_4 = \mathbf{MgNH_4PO_4} + Na_2SO_4 + H_2O$$

cf. Magnesium

$$Na_2HAsO_4 + \text{"} + MgSO_4 = \mathbf{MgNH_4AsO_4} + \text{"} + \text{"}$$

$$Na_2HPO_4 + FeCl_3 = \mathbf{FePO_4} + 2NaCl + HCl$$

$$Na_2HAsO_4 + \text{"} = \mathbf{2FeAsO_4} + \text{"} + \text{"}$$

Sodium acetate ($NaC_2H_3O_2$) must be present to prevent the formation of free HCl in which $FePO_4$ and $FeAsO_4$ are soluble.

$$Na_2HPO_4 + 3AgNO_3 + NH_4HO = \mathbf{Ag_3PO_4} + NaNO_3 + NH_4NO_3 + H_2O$$

The phosphates of potassium, sodium, and ammonium are soluble in water. The acid phosphates are also soluble.

The normal phosphates, except those above mentioned, are not soluble in water, but can usually be dissolved in acids.

Chromates (using $K_2Cr_2O_7$ or K_2CrO_4).

$$\underset{[K_2O.2CrO_3]}{K_2Cr_2O_7} + \underset{[H_2O.SO_3]}{4H_2SO_4} + 3H_2S = \underset{[K_2O.SO_3]}{K_2SO_4} + \underset{[Cr_2O_3.3SO_3]}{Cr_2(SO_4)_3} + 7H_2O + \mathbf{S_3}$$

$$K_2Cr_2O_7 + 8HCl + 3H_2S = 2KCl + 2CrCl_3 + 7H_2O + \mathbf{S_3}$$

$$\text{"} + \text{"} + 3\underset{[\text{Ethyl Alcohol}]}{CH_3CH_2OH} = \text{"} + \text{"} + \text{"} + 3\underset{[\text{Aldehyde}]}{CH_3CHO}$$

See equations on p. 10 also.

For reactions with salts of Silver, Lead and Barium, see *ante*.

The more common soluble chromates and bichromates are—K_2CrO_4, $K_2Cr_2O_7$, Na_2CrO_4, $Na_2Cr_2O_7$, $(NH_4)_2CrO_4$, $(NH_4)_2Cr_2O_7$.

The soluble normal chromates are yellow.

Dilute acids convert the normal chromates into orange-coloured bichromates.

$$2K_2CrO_4 + H_2SO_4 = K_2Cr_2O_7 + K_2SO_4 + H_2O.$$

Reducing agents (H_2S, H_2SO_3, C_2H_5OH, $SnCl_2$), in presence of an excess of acid, convert chromates or bichromates into chromic salts.

Oxalates (using $(NH_4)_2C_2O_4$).

$$(NH_4)_2C_2O_4 + H_2SO_4 \text{ (concentrated)} = (NH_4)_2SO_4 + CO + CO_2$$

$$\text{"} + MnO_2 + 2H_2SO_4 = MnSO_4 + (NH_4)_2SO_4 + 2H_2O + 2CO_2$$

$$\text{"} + CaCl_2 = \mathbf{CaC_2O_4} + 2NH_4Cl$$

Potassium, sodium, and ammonium oxalates are soluble in water.

REACTIONS FOR THE ACID-RADICLES.

GROUP II.—BORIC,(1) SULPHURIC, PHOSPHORIC, CHROMIC AND OXALIC.

Use the potassium or sodium salt of the acid for applying the tests.

Reagent Employed.	Boric.	Sulphuric.	Phosphoric.	Chromic.	Oxalic.
$BaCl_2$	White ppt. sol. in HCl, and in NH_4Cl.	White ppt. insol. in HCl.	White ppt. sol. in HCl, in HNO_3 or in $H\bar{A}$.	Yellowish white ppt. ($BaCrO_4$) sol. in HCl but insol. in $H\bar{A}$.	White ppt. in neutral solutions, sol. in HCl but insol. in $H\bar{A}$.
$AgNO_3$	———	———	Yellow ppt. sol. in HNO_3 & in NH_4HO.	Red ppt. (Ag_2CrO_4) sol. in HNO_3 and in NH_4HO.	———
$Pb2C_2H_3O_2$	White ppt.	(2)White ppt. sol. in KHO and in boiling HCl.	White ppt.	Yellow ppt. sol. in KHO, insol. in $H\bar{A}$.	White ppt. sol. in HNO_3.
$FeCl_3$ and $Na\bar{A}$	———	———	Yellow ppt. of $FePO_4$ sol. in HCl and in excess of $FeCl_3$.	———	———
NH_4HMoO_4 and HNO_3	———	———	Yellow ppt. on warming gently.	———	———
NH_4Cl, NH_4HO and $MgSO_4$	———	———	White cryst. ppt. sol. in HCl.	———	———
$KMnO_4$ and a drop of H_2SO_4	———	———	———	———	Colour destroyed on warming.
H_2S	———	———	———	Soln. turns green and sulphur is precipitated.(3)	———
MnO_2(4) and H_2SO_4	———	———	———	———	Evolution of CO_2 which will ppt. $CaCO_3$ from lime-water.
Flame test (substance moistened with H_2SO_4 and held *close to* lower edge of bunsen flame)	Green colour due to liberated boric acid.	———	———	———	———

(1) Often called Boracic acid.
(2) See note on page 5.
(3) See pages 10 and 18.
(4) Black type used to indicate dry reagents.

$$KCl + AgNO_3 = AgCl$$
$$KBr + AgNO_3 = AgBr + KNO_3$$
$$KI + AgNO_3 = AgI$$

$$2KCl + 2KBr + MnO_2 + 2H_2SO_4 = MnSO_4 + K_2SO_4 + 2H_2O + Cl_2 + Br_2$$

$$2KI + MnO_2 + 2H_2SO_4 = MnSO_4 + K_2SO_4 + 2H_2O + I_2$$

$$2KI + Cl_2 \text{ (chlorine water)} = 2KCl + I_2$$

The *free* Iodine imparts a blue colour to starch.

Solid chlorides with $K_2Cr_2O_7$ and concentrated H_2SO_4 yield CrO_2Cl_2, Oxychloride of Chromium, sometimes called Chlorochromic Acid.

$$4NaCl + K_2Cr_2O_7 + 6H_2SO_4 = 2CrO_2Cl_2 + 4NaHSO_4 + 3KHSO_4 + 3H_2O$$

This reacts with water to form Chromic Acid and Hydrochloric Acid

$$CrO_2Cl_2 + 2H_2O = H_2CrO_4 + 2HCl$$

Bromides with $K_2Cr_2O_7$ and H_2SO_4 yield free Bromine

$$6KBr + K_2Cr_2O_7 + 11H_2SO_4 = 3Br_2 + Cr_2(SO_4)_3 + 8KHSO_4 + 7H_2O$$

For reactions of Iodides with salts of Lead and Mercury see *ante*.

The only common insoluble chlorides are—AgCl, Hg_2Cl_2, $PbCl_2$, Cu_2Cl_2. All the other chlorides are soluble in water, $PbCl_2$ is slightly soluble in cold and very soluble in hot water, from which it crystallises out on cooling.

The most common insoluble bromides are AgBr and Hg_2Br_2. All the other common bromides are soluble in water.

All the common iodides are soluble in water. PbI_2 is only very slightly soluble in cold but readily soluble in hot water, from which it crystallises out on cooling. HgI_2 is insoluble in water but soluble in KI. (See *ante*).

NITRATES (using KNO_3).

$$6FeSO_4 + 5H_2SO_4 + 2KNO_3 = 3Fe_2(SO_4)_3 + 2KHSO_4 + 4H_2O + 2NO$$ (See note [1] on p. 21).

All the common nitrates are soluble in water except $Bi(NO_3)_3$, which is decomposed, forming insoluble $(BiO)NO_3$.

CHLORATES (using $KClO_3$).

DANGEROUS

$$3KClO_3 + H_2SO_4 = KClO_4 + K_2SO_4 + H_2O + Cl_2O_4$$
$$6 \text{ " } + 3 \text{ " } = 2HClO_4 + 2K_2SO_4 + 2H_2O + 2Cl_2O_4$$

All the common chlorates are soluble in water.

Table of Differences.

Halogen Group.
Nitric Acid Group.

REACTIONS FOR THE ACID-RADICLES.

GROUP III.—HYDROCHLORIC, HYDROBROMIC AND HYDRIODIC.

Reagent Employed.	Hydrochloric.	Hydrobromic.	Hydriodic.
$AgNO_3$ and a drop of HNO_3.	White ppt. sol. in NH_4HO: ppt. reappears on the addition of HNO_3. If the ppt. of AgCl is heated it coagulates and turns dark coloured on standing.	White or yellowish ppt. sparingly sol. in NH_4HO.	Yellow ppt. insol. in NH_4HO.
Solid salt with $K_2Cr_2O_7$ and conc. H_2SO_4 gives on warming.	Red gas evolved, condensing easily to a liquid (CrO_2Cl_2).	Reddish fumes of Bromine evolved.	——
MnO_2 and H_2SO_4.	Chlorine evolved.	Bromine evolved.	Iodine evolved.
Starch and chlorine water.	No change.	Yellow colouration.	Deep blue colouration.
$Hg''Cl_2$.	——	——	Yellow or salmon coloured ppt. sol. in excess of either reagent.

GROUP IV.—NITRIC AND CHLORIC.

Reagent Employed.	Nitric.	Chloric.
Ferrous sulphate ($FeSO_4$) and H_2SO_4.	"Brown ring" test.[1]	——
Metallic copper and H_2SO_4.	Red fumes evolved on warming.[2]	No red fumes evolved.
Sulphate of indigo and H_2SO_4.	Colour destroyed on warming.	Colour destroyed in the cold if some Na_2SO_3 is added to the mixture.
Strong H_2SO_4 on a *small* fragment of the salt.	——	Yellowish, sweet smelling gas evolved, accompanied by sharp explosions. [DANGEROUS].
Phenyl sulphate and H_2SO_4 to crystal on a watch glass.	Brownish red colouration becoming yellow or green on the addition of NH_4HO.	——
Aniline sulphate and H_2SO_4 to solid as above.	——	Intense blue colour produced.

(1) To do the "brown ring" test take about three-quarters of an inch of the solution of nitrate in a test-tube, incline the tube and add cautiously about the same volume of a fresh solution of ferrous sulphate ($FeSO_4$), pouring it down the side of the tube so that it forms a layer on the top of the nitrate. Then add, in the same manner, some concentrated sulphuric acid, which will run down the side of the tube to below the nitrate solution. Free nitric acid is thus produced by the action of the sulphuric acid on the nitrate, and in contact with the ferrous sulphate it becomes reduced to nitric oxide; the nitric oxide unites with the excess of ferrous sulphate present to form a brown compound, $(FeSO_4)_2NO$. This compound is only stable in the cold. In analytical work, should the base present cause a precipitate of an insoluble sulphate, such precipitate will not interfere with the production of the brown ring which can readily be seen through it.

(2) The sulphuric acid liberates nitric acid from the nitrate and this reacts with the copper yielding nitric oxide.

CYANIDES (using KCN).

$$AgNO_3 + KCN = \mathbf{AgCN} + KNO_3$$

"Prussian Blue" reactions:

(1) $6KCN + 3FeCl_3 = \mathbf{3Fe2CN} + 6KCl$

(2) $\mathbf{3Fe2CN} + 4KHO = K_4Fe6CN + \mathbf{2Fe(OH)_2}$

(3) $3K_4Fe6CN + 4FeCl_3 = \mathbf{(Fe_2)_3(Fe6CN)_4} + 12KCl$

or, expressing all the reactions in one equation:

$$18KCN + 3FeCl_2 + 4FeCl_3 = \mathbf{(Fe_4)_3(Fe6CN)_4} + 18KCl$$

$$2HCN + (NH_4)_2S + S_2 = 2NH_4CNS + H_2S$$

HCy, KCy, NaCy, NH_4Cy, and $HgCy_2$ are soluble in water.

The cyanides are decomposed by strong acids, HCy being given off.

The most common soluble ferrocyanides are—K_4FeCy_6, Na_4FeCy_6, $(NH_4)_4FeCy_6$.

K_3FeCy_6 is the most common soluble ferricyanide.

ACETATES (using $NaC_2H_3O_2$).

$$3NaC_2H_3O_2 + FeCl_3 = Fe3C_2H_3O_2 + 3NaCl$$

$$NaC_2H_3O_2 + NaHO \text{ [heated dry]} = Na_2CO_3 + CH_4$$

$$\begin{cases} 2NaC_2H_3O_2 + H_2SO_4 = 2HC_2H_3O_2 + Na_2SO_4 \\ C_2H_5HO + \text{"} = C_2H_5HSO_4 + H_2O \\ HC_2H_3O_2 + C_2H_5HSO_4 = (C_2H_5)C_2H_3O_2 + H_2SO_4 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{[Ethyl Acetate]} \end{cases}$$

All the common acetates are soluble in water.

REACTIONS FOR THE ACID-RADICLES.

GROUP V.—HYDROCYANIC, HYDROFERROCYANIC, HYDROFERRICYANIC, SULPHOCYANIC AND ACETIC.

NOTE.—This and the following series of acids do not form well defined groups.

REAGENT EMPLOYED.	HYDROCYANIC. (HCN)	HYDROFERROCYANIC. (H_4Fe6CN)	HYDROFERRICYANIC. (H_3Fe6CN)	SULPHOCYANIC. (HCNS)	ACETIC. ($HC_2H_3O_2$)
$AgNO_3$.	White ppt. of AgCN insol. in HNO_3, sparingly in NH_4HO, readily in KCN.	White ppt. of Ag_4Fe6CN insol. in HNO_3 and in NH_4HO; changes to orange red on warming with HNO_3.	Orange red ppt. sol. in NH_4HO. [*Notice* solubility in NH_4HO].	White ppt. of AgCNS sol. in NH_4HO.	White ppt. in strong solutions, sol. in NH_4HO.
$CuSO_4$.	——	Chocolate red ppt. of Cu_2Fe6CN. (Very delicate reaction).	Yellowish ppt.	Black ppt. of Cu2CNS changing on standing to CuCNS.	——
$FeCl_3$.	——	Dark blue ppt. of "Prussian Blue."	Dark green colouration but no ppt.	Blood red colouration of Fe3CNS unchanged by HCl.	Deep red colouration changed to yellow by HCl. If soln. is made alkaline with KHO and boiled the whole of the iron is ppt. as *basic acetate*.
A drop of KHO, then a few drops of $FeSO_4$ and of $FeCl_3$ and soln. boiled.	On acidifying with HCl—dark blue ppt. of "Prussian Blue."	——	——	——	——
Warmed with *yellow* $(NH_4)_2S$ in a porcelain basin till soln. is colourless, then HCl and $FeCl_3$ added.	Blood red colouration.	——	——	——	——
Warmed with alcohol and strong H_2SO_4.	——	——	——	——	Odour of Ethyl Acetate. ($C_2H_5C_2H_3O_2$)
Warmed with HCl or H_2SO_4.	——	——	——	——	Odour of Acetic Acid.

TARTRATES.

$H_2C_4H_4O_6$, $KHC_4H_4O_6$, $NaHC_4H_4O_6$, $(NH_4)HC_4H_4O_6$, and $K(SbO)C_4H_4O_6$ (tartar emetic) are soluble in water.

HYPOCHLORITES (using Ca2ClO or $CaOCl_2$).

$$\begin{cases} Ca2ClO + 2HCl = CaCl_2 + 2HClO \\ HClO + HCl = H_2O + Cl_2 \end{cases}$$

$$CaOCl_2 + 2HCl = CaCl_2 + H_2O + Cl_2$$

KClO, NaClO, Ca2ClO and Mg2ClO are the most common soluble hypochlorites. The hypochlorites are usually accompanied by chlorides, as in bleaching powder, $CaCl_2Ca2ClO$.

NITRITES (using KNO_2).

$$2KNO_2 + H_2SO_4 = K_2SO_4 + H_2O + N_2O_2 \text{ (brown fumes)}$$

All the common nitrites are soluble in water.

BENZOATES AND SALICYLATES (using $C_6H_5CO_2Na$ and $C_6H_4(OH)CO_2Na$).

Separation of the acids, which are sparingly soluble in water, on addition of HCl or H_2SO_4:

$$C_6H_5CO_2Na + HCl = C_6H_5CO_2H + NaCl$$
$$C_6H_4(OH)CO_2Na + \text{"} = C_6H_4(OH)CO_2H + NaCl$$

Decomposition on heating with an alkali:

$$C_6H_5CO_2H = C_6H_6 + CO_2$$
$$C_6H_4(OH)CO_2H = C_6H_5(OH) + CO_2$$

Benzoic acid and salicylic acid are only slightly soluble in water, but readily dissolve in solutions of potassic or sodic hydrates to form benzoates or salicylates.

REACTIONS FOR THE ACID-RADICLES.

GROUP VI.—TARTARIC, HYPOCHLOROUS, NITROUS, BENZOIC AND SALICYLIC.

Reagent Employed.	Tartaric. ($H_2C_4H_4O_6$)	Hypochlorous. (HClO)	Nitrous. (HNO_2)	Benzoic. ($HC_7H_5O_2$)	Salicylic. ($HC_7H_5O_3$)
H_2SO_4 (*concentrated*)	Substance blackens.	Chlorine is liberated.	Red fumes evolved.	Benzoic acid is precipitated.	The acid is precipitated.
$AgNO_3$	White ppt. in neutral solns. sol. in NH_4HO and in HNO_3.	White ppt.	White ppt. sol. in a large excess of water.	——	——
Strong KCl or KNO_3	White cryst. ppt. on shaking; sol. in excess of water, insol. in alcohol.	——	——	——	——
$FeSO_4$	——	——	Brown or black colouration, destroyed by boiling	——	——
$FeCl_3$	——	——	——	Buff coloured ppt. sol. in HCl with liberation of *white* benzoic acid.	Deep violet colouration, destroyed by HCl.
Heated with **KHO** or **soda-lime.**	——	——	——	Smell of benzene.	Smell of carbolic acid [phenol].
Heated on platinum foil or on a porcelain crucible lid.	Chars, evolving a smell of burnt sugar.	——	Unaffected by heat.	Characteristic smell of benzoic acid.	——

MISCELLANEOUS.

Fluorides (using CaF_2).

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$$

Phenol, or Carbolic Acid.

$$C_6H_5(OH) + 3Br_2 = C_6H_2Br_3OH + 3HBr$$

[Tribrom-phenol]

Alcohol.

Formation of Iodoform from Alcohol, Potassium Hydrate and Iodine:

$$\begin{cases} CH_3CH_2OH + I_2 = CH_3CHO + 2HI \\ CH_3CHO + 3I_2 = CI_3CHO + 3HI \\ CI_3CHO + KHO = CHI_3 + HCO_2Na \end{cases}$$

Action of the Metals on the Common Acids, Hydrochloric, Nitric, Sulphuric.

With Hydrochloric Acid.

$$(Cu, Cd, Sn, Fe, Zn, Ni, Co, or Mg) + 2HCl = (Cu, Cd, Sn, Fe, Zn, Ni, Co, or Mg)Cl_2 + H_2$$

With Nitric Acid.

The amount of the deoxidation of HNO_3 by the metals differs. Tin and Antimony take away the least, then Silver and Mercury, Copper, etc. still more; Zinc most of all.

$$Sn + 4HNO_3 = SnO_2 + 2H_2O + 2N_2O_4$$

$$2Sb + 10HNO_3 = Sb_2O_5 + 5H_2O + 5N_2O_4$$

$$4(Ag, Hg) + 6HNO_3 = 4(Ag, Hg')NO_3 + 3H_2O + N_2O_3$$

$$As_4 + 10HNO_3 + H_2O = 4H_3AsO_4 + 5N_2O_3$$

$$3(Cu, Hg, Pb, Cd, Ni, Co, Mg) + 8HNO_3 = 3(Cu, etc.)2NO_3 + 4H_2O + N_2O_2$$

$$2(Bi, Fe, Al) + 8HNO_3 = 2(Bi, Fe, Al)3NO_3 + 4H_2O + N_2O_2$$

$$4Zn + 10HNO_3 = 4Zn2NO_3 + 5H_2O + N_2O$$

With Sulphuric Acid.

$$(Cu, Hg, Pb) + 2H_2SO_4 = (Cu, Hg, Pb)SO_4 + 2H_2O + SO_2$$

$$Ag_2 + \text{〃} = Ag_2SO_4 + \text{〃} + \text{〃}$$

$$Bi_2 + 6H_2SO_4 = Bi_2{}^{VI}3SO_4 + 6H_2O + 3SO_2$$

$$Sn + 3H_2SO_4 = Sn^{IV}2SO_4 + 4H_2O + 2SO_2$$

$$(Zn. Mn, Ni, Co, Fe, Cd, Mg) + H_2SO_4 (dilute) = (Zn, etc.)SO_4 + H_2$$

DETECTION OF SIMPLE SALTS.

The student having gone over the tests for the metals and acid radicles is now in a position to apply those tests to the systematic examination of an unknown substance. The first set of analytical tables, if followed carefully, will serve for the detection of the great majority of simple salts. When mixtures of several are to be examined the "Tables of Separation" must be used, but the general principles on which these are framed are similar to those for one base, or metal, and one acid. The order in which the group reagents are added is of prime importance as each one of these is selected so as to separate all of its own particular group from those groups that follow and *not* from those groups that precede it. For example, were the metals of group I not removed by hydrochloric acid they would all be precipitated as sulphides along with those of group II.

An unknown substance being given for examination its appearance should be noted and a preliminary flame-test applied: it should be heated on a piece of iron or platinum foil and its behaviour noticed in so far as it may char or give off some characteristic smell, or even volatilize completely. This treatment will often tell if it is an organic substance or the salt of an organic acid and usually gives some clue as to the composition of the body. It should then be got into solution, in water if possible. If it appears quite insoluble on boiling with water then hydrochloric acid should be employed but *not* nitric acid, unless there are facilities for driving off all excess of nitric acid by evaporating to dryness, as this causes a precipitation of sulphur when hydrogen sulphide comes to be used for the precipitation of group II. In this process of solution in hydrochloric acid should any one of the volatile acids under the heading I. on page 17 be present it will be readily identified at this stage. The student should make a concentrated solution of the substance under examination and use only portions of this, suitably diluted, for his subsequent tests. The result of the exrmination of each salt should be entered in the note-book somewhat in the following form:

SPECIMEN PAGE FROM STUDENT'S NOTE BOOK.

October 29.

No. 6.—White solid, sol. in cold water.

For *base*.

O.S. and dil. HCl.	no ppt.	group I absent.
O.S. with HCl and H_2S	black ppt.	group II present.
Ppt. warmed with NH_4OH and $(NH_4)_2S$	ppt. insol.	group II.a present.
O.S. and dil. H_2SO_4	no ppt.	lead absent.
Same sol. and KOH	yellow ppt.	mercury (ic) present.
O.S. and $SnCl_2$	white ppt. turning grey	" "
O.S. and KI	red ppt.	" "
O.S. and NH_4OH	white ppt.	" "

For *acid*.

Preliminary test indicated nothing.		
O.S. and HCl	no effervescence or gas evolved	
No borate found by flame test.		
O.S. and $BaCl_2$	no ppt.	group II absent.
O.S. with HNO_3 and $AgNO_3$	white ppt. readily sol. in NH_4HO	group IV present.
O.S. with MnO_2 and H_2SO_4	greenish gas evolved	hydrochloric acid present.

Substance is Mercuric Chloride ($HgCl_2$).

Analytical Table for One Base.

I. To original solution (to be called "O.S." hereafter) of substance[1] add Hydrochloric Acid[1] drop by drop till no further change occurs; a ppt. produced indicates presence of Gp. I. [Ascertain that ppt. is not due to the separation of insoluble organic acids such as Salicylic or Benzoic].

To ppt. add NH_4HO[1].

ppt. dissolves *Silver*	ppt. blackens *Mercury* (-ous).	ppt. insoluble. *Lead*
[2] Confirm in O.S. with K_2CrO_4.	Conform in O.S. with $SnCl_2$—white or grey ppt.	Confirm (1) by dissolving ppt. in hot water; (2) by K_2CrO_4.

II. No precipitate with HCl; to *same* solution add sulphuretted hydrogen (H_2S), boiling solution and adding more of the reagent till no further change takes place. A precipitate indicates presence of Gp. II.

To a portion of the ppt. add NH_4HO and $(NH_4)_2S$ and warm—ppt. insoluble—Gp. II. *a*; ppt. dissolves Gp. II. *b*.*

(*a*) The ppt. produced by H_2S was brown or black, to O.S. add H_2SO_4 (dil).

White ppt. *Lead* Confirm in O.S. with KI and with K_2CrO_4	No ppt.; to same solution add KHO			The H_2S ppt. was yellow. *Cadmium* Confirm in O.S. with KHO.
	White ppt. *Bismuth* Confirm in O.S. by adding excess of water.	Yellow ppt. To O.S. add NH_4HO, white ppt. *Mercury* (-ic) Confirm in O.S. with KI and with $SnCl_2$.	Blue ppt. *Copper* Confirm in O.S. with NH_4HO and with K_4Fe6CN.	

* (*b*) The ppt. produced by H_2S is soluble in NH_4HO and $(NH_4)_2S$.

The ppt. was brown *Tin* (Stannous). Confirm in O.S. with $HgCl_2$	The ppt. was orange. *Antimony*	The ppt. was yellow; to O.S. add KHO.	
		White ppt. soluble in excess of KHO *Tin* (Stannic).	No ppt.; to O.S. add $CuSO_4$ to which NH_4HO has been previously added until the blue ppt. at first formed just redissolves.
			Pale green ppt. *Arsenic* (-ous) Confirm in O.S. with $AgNO_3$
			Pale blue ppt. *Arsenic* (-ic). Confirm in O.S. with $AgNO_3$.

(1) See foot note on page 5. Care should be taken not to add too much hydrochloric acid as cadmium sulphide is soluble in a 5% solution of this acid and might therefore not be precipitated when hydrogen sulphide is added to precipitate Group II. Other sulphides of the second group are also soluble in *hot* dilute hydrochloric acid so any excess of acid, other than what is required to precipitate Group I, must be carefully avoided.

(2) In doing all confirmatory tests refer back to where these tests are given in the Tables of Differences.

III. No. ppt. with H_2S; to O.S.* add NH_4Cl and NH_4HO in excess and warm. Ppt.—Gp. III.*a*. **Bases, 3, 4, and 5.**

The ppt. in greenish black.	The ppt. is reddish brown.	The ppt. is white or a transparent white.	The ppt. is dirty green.
Ferrous. Confirm in O.S. by K_4Fe6CN.	*Ferric.* Confirm in O.S. with K_4Fe6CN and with KCNS.	*Aluminum.* Confirm in O.S. by KHO, white ppt. soluble in excess and repptd. on addition of NH_4Cl.	*Chromium.* Confirm in O.S.* by KHO.

**Note.*—If solution has changed from yellow or orange to green or purple during the passing of H_2S gas, then add NH_4Cl and NH_4HO to *that* solution instead of to original solution. . . This would indicate the presence of Chromic Acid originally, which had been reduced by the H_2S according to the equation $K_2Cr_2O_7 + 8\ HCl + 3\ H_2S = 2\ KCl + 2CrCl_3 + 7\ H_2O + S_3$.

Gp. III.*b*. No. ppt. with NH_4Cl and NH_4HO; to *same* solution add $(NH_4)_2S$.(1) Ppt. Zn. Mn. Ni. Co.

Ppt. is white.	Ppt. is brownish white or pink.	Ppt. is black; to O.S. add NH_4HO.	
Zinc. Confirm in O.S. with KHO —White ppt. soluble in excess and repptd. by H_2S.	*Manganese.* Confirm in O.S. by KHO, or by Pb_3O_4 test.	Bluish green ppt. soluble in excess. *Nickel.* Confirm in O.S. with KHO and bromine water.	Bluish green ppt. soluble in excess. *Cobalt.* If O.S. was pink, cobalt is confirmed.

Gp. IV. No ppt. with $(NH_4)_2S$; to *same* solution add $(NH_4)_2CO_3$—ppt. Ba. Sr. Ca. To O.S. add $CaSO_4$ and warm.

White ppt. appearing at once.	White ppt. appearing after some time if solution is dilute.	No. ppt.
Barium. Confirm by flame—Green.	*Strontium.* Confirm by flame—Crimson.	*Calcium.* Confirm by flame—Orange Red.

Gp. IV.*b*. No. ppt. with $(NH_4)_2CO_3$; to O.S. add NHCl, NH_4HO and Na_2HPO_4. A white crystalline ppt. indicates presence of *Magnesium*.

Gp. V. No. ppt. with Na_2HPO_4; to O.S. add KHO and warm.

Smell of NH_3.	No odour of NH_3; test in O.S. for *Potassium* and *Sodium*, by flame tests.
Ammonium.	

(1) Only *a drop or two at a time* should be added, the mixture shaken, and the precipitate observed carefully; ammonium sulphide is often yellow in colour and consequently the white or light-coloured sulphides of zinc and of manganese *appear to be coloured* if much reagent is added.

Analytical Scheme for the Detection of One Acid in a Salt.

It must be remembered that many of the following tests may be interfered with by the *base* being other than an *alkali*. The student must therefore use his own judgment in interpreting his results. Should it be desired, the *base* may be removed from the substance under analysis by boiling with sodium carbonate, which will precipitate the carbonate of the base and leave the sodium salt of the acid in solution.

Preliminary Tests.

1. Place a little of original substance on a piece of foil, or on a porcelain crucible lid, and heat over bunsen flame; if substace blackens or chars, an organic acid is probably present.

2. To original *substance* add a little concentrated H_2SO_4, skake, and notice if any odour is produced. If not, heat the mixture:

Odour of Burning Sulphur	indicates	Sulphurous Acid	H_2SO_3.
" " " and Sulphur pptd	"	Thiosulphuric "	$H_2S_2O_3$.
" Vinegar	"	Acetic "	$HC_2H_3O_2$.
" Sulphuretted Hydrogen	"	Hydrosulphuric "	H_2S.
" Bitter Almonds	"	Hydrocyanic "	HCN.
" Chlorine	"	Hypochlorous "	$HClO$.
" Chlorous Compounds and liquid turns yellow†	"	Chloric "	$HClO_3$.
Odourless or slightly acidulous gas given off	"	Carbonic "	H_2CO_3.
Substance chars and gives odour of SO_2 and of Burnt Sugar	"	Tartaric "	$H_2C_4H_4O_6$.
Reddish gas evolved	"	Nitrous "	HNO_2.
Acid fumes evolved	"	Hydrochloric or Nitric "	HCl or HNO_3.
Brown vapours evolved	"	Hydrobromic "	HBr.
Violet vapours evolved	"	Hydriodic "	HI.
Aromatic irritating vapours evolved	"	Benzoic "	$C_6H_5CO_2H$.

Note.—A Precipitate produced by addition of H_2SO_4 is probable due to the *base* with which the acid is combined, or to the separation of insoluble acids, such as Benzoic or Salicylic, and need not interfere with the preliminary tests.

Two much dependence must not be placed on these preliminary tests as they are only intended to give some *indication* of what the acid combined with the base, already detected, *may* be. It will be noticed that only a few of the acids contained in the tables that follow are given here. The beginner will find it difficult to distinguish between the various odours and should not take up much time over these tests but proceed to the systematic examination described on the next two pages.

Traces of chlorides and sulphates are continually met with, and the student should be able to discriminate by the appearance of the precipitate whether or no these are mere impurities in the salt.

† DANGEROUS!

Acids, 1, 2, 3 and 4.

I. After preliminary tests; to O.S. if soluble (or to original substance suspended in water if insoluble) add Hydrochloric Acid and warm.

Effervescence. *Carbonic.* Confirm with lime-water ($Ca(OH)_2$).	Smell of Sulphuretted Hydrogen. *Hydrosulphuric.* Confirm with paper moistened with a soluble lead salt.	Smell of Burning Sulphur. *Sulphurous.* Confirm with paper moistened with K_2CrO_4.	Smell of Burning Sulphur and white ppt. of Sulphur. *Thiosulphuric.* Confirm.	Reddish coloured gas evolved. *Nitrous.* Confirm in O.S. with $FeSO_4$—brown colouration.

II. No odour or effervescence with HCl; moisten original substance with a drop of concentrated H_2SO_4 and test for a *Borate* by flame test.(1)

III. No Borate present; to O.S. add $BaCl_2$, (or $Ba2NO_3$ if Lead, Silver or Mercury (*—ous*) has been found in testing for the *base*.)

Yellow ppt. *Chromic.* Confirm in O.S. with H_2S or with $AgNO_3$ or PbA_2	White ppt. insoluble in HCl. *Sulphuric.* Confirm in O.S. with PbA_2—White ppt.; *this precipitate* ($PbSO_4$) is soluble in KHO.(1)	White ppt. insoluble in HCl. *Phosphoric.* Confirm in O.S. with NH_4Cl, NH_4HO, and $MgSO_4$—White cryst. ppt.	White ppt. soluble in HCl. *Oxalic.* Confirm in O.S. with $CaCl_2$—White ppt. insoluble in Acetic Acid. Or with MnO_2 and H_2SO_4 —CO_2 evolved.	White ppt. *Boric.* Already detected by flame test.

IV. No ppt. with $BaCl_2$; to O.S. add a few drops of HNO_3 and then $AgNO_3$. A white or yellow ppt. of the chloride, bromide or iodide of silver is formed.

To the precipitate add NH_4HO in excess:

Ppt. dissolves readily. *Hydrochloric.*	Ppt. dissolves with difficulty. *Hydrobromic.*	Ppt. is insoluble. *Hydriodic.*

The presence of a chloride, bromide or iodide should be confirmed by (*a*) the starch and chlorine-water reaction, (*b*) the MnO_2 and H_2SO_4 reaction: (see table of differences).

Note.—A *cyanide* or a *nitrite* also yields an insoluble silver salt with $AgNO_3$. If the substance under examination is found not to be a salt of one of the halogen acids, apply tests for these two to O.S. (See tables of differences).

(1) As soluble borates give a precipitate of barium borate closely resembling the insoluble barium salts of the succeeding group of acids (III), they must be tested for separately at this stage; hence the introduction into the table of (II).

(2) See note on p. 5.

V. No precipitate with HNO_3 and $AgNO_3$; to a *small* portion of the solid salt under examination, add H_2SO_4 (conc), mix well and heat:

Yellow gas evolved.	Odour of Vinegar.	Acid or slightly acid fumes.
DANGEROUS! *Chloric.*	*Acetic.*	*Nitric.*
Confirm in O.S. with Sulph. Indigo, H_2SO_4 and Na_2SO_3.	Confirm in O.S. with $FeCl_3$, or with alcohol and H_2SO_4.	Confirm in O.S. with "Brown Ring" test, or with Sulph. Indigo and H_2SO_4.

If the above acids are absent, to O.S. add $FeCl_3$.

Buff coloured ppt.	Deep violet colouration destroyed by HCl.	No ppt. Heat some of solid substance; charring with a smell of burnt sugar indicates presence of
Benzoic.	*Salicylic.*	*Tartaric.*
Confirm by some of the tests given in Table of Differences.	Confirm by some of the tests given in Table of Differences.	

NOTE: Occasionally a metallic oxide may be given for analysis. With the exception of the oxides of the alkalies they are all practically insoluble in water; those of the alkaline-earths are sparingly soluble, yielding the common laboratory reagents lime-water and baryta-water, (strontia-water is not used). The oxide of arsenic, As_2O_3, though apparently insoluble in cold water, yields a solution on boiling which readily gives the reactions for arsenic. In the systematic examination of an oxide by the foregoing tables, it will have been got into solution by treatment with hydrochloric acid, consequently the students' "original solution" will contain the *chloride* of the base and free hydrochloric acid. It is useless, therefore, to go through the analytical tables to find out what acid is in the salt for only the reactions for a chloride will be obtained. A knowledge of the physical properties, such as the solubility in water or otherwise, (to be found on the pages having *even* numbers) will, after a little practice, enable the student to tell if he has made a mistake in his analysis or to definitely conclude that the substance must be the oxide of the metal. For example, the body you are analysing is (say) a black powder, insoluble in water but soluble on boiling with hydrochloric acid without the evolution of any characteristic gases such as those mentioned in Group I of the acids, and you find by your tables that the base is copper. If the original solution be examined for the acid radicles hydrochloric acid will be found and the conclusion probably jumped at that the substance was copper chloride. But experience and the description of the salts of copper given on page 6, shew that copper chloride is a blue soluble salt, whereas this was black and insoluble in water. Hence, the body under examination must be the oxide.

Skeleton Tables for the SEPARATION of the BASES when more than one are present.

The group reagents are employed here in exactly the same way as in testing for a single base. *Precipitation must in every case be complete and each group precipitate must be thoroughly washed on the filter with hot water and the first of the washings added to the filtrate.* The filtrates are kept to be subsequently examined for the succeeding group or groups. In all cases confirmatory tests should be made.

Group I.—Separation of Silver, Mercury ("ous") and Lead.

1. The Group I. ppt. (produced by the addition of hydrochloric acid to O.S.) is boiled with water and filtered hot.

- **Filtrate may contain** *Lead*
- **Residue:** Digest with warm ammonia on the filter
  - **Filtrate may contain** *Silver*
  - **Residue (black)** *Mercury* — Confirm by mixing with a little solid Na_2CO_3 and heating in a small hard glass tube when small globules of metallic mercury will be seen on its walls.

Group IIa. Separation of Lead, Mercury, Bismuth, Copper, Cadium.

The Group II ppt. (produced by passing hydrogen sulphide through the filtrate from Group I, boiling the liquid, again passing H_2S and boiling till no further precipitate is obtained) is washed with hot water. [In order to separate the elements of Group II (*b*) viz. arsenic, antimony and tin, from those of Group II (*a*) the ppt. must be digested with ammonia and ammonium sulphide which dissolves them out. This solution and washings are kept for further examination.]†

II. (*a*) The ppt. containing only the sulphides of the Group II (*a*) metals is washed and boiled with nitric acid, diluted and filtered.

- **Residue:** *Mercury* — Dissolve in Aqua Regia and confirm with $SnCl_2$
- **Filtrate:** Add H_2SO_4 (dilute)
  - **Precipitate** *Lead*
  - **Filtrate:** Add NH_4HO
    - **Precipitate** *Bismuth*
    - **Filtrate***
      - **Residue** *Copper* — Wash, dissolve by hot HCl and confirm.
      - **Filtrate** *Cadmium* — Confirm by diluting with water and adding H_2S.

* To filtrate add HCl till acid, and precipitate as sulphides with hydrogen sulphide; wash, add dilute H_2SO_4, boil and filter *quickly*.

† *Note:* for the separation of arsenic, antimony and tin see any larger work on qualitative analysis. The student will therefore omit, in the meantime, the instructions contained within the heavy brackets above.

Separation of the Bases. Group III (a) and (b).

Note.—This table is only applicable in the absence of phosphates.

The filtrate from Group II. is boiled to expel hydrogen sulphide, a few drops of concentrated nitric acid added and the solution again boiled. Ammonium chloride is added, then ammonia in excess and the whole heated to boiling once more. Filter *quickly* and wash precipitate thoroughly, adding washings to the filtrate which will contain the metals of Group III. (*b*) *et seq.*

III. (a) The precipitate may contain $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$ . . . . . III. (*a*),

Divide precipitate into three parts, *a*, *b* and *c*, and test each portion separately as follows:

(*a*) Dry and fuse on a crucible lid with solid $NaHCO_3$ and a little solid KNO_3. Cool, and extract the fused mass with water, filter from insoluble residue, acidify filtrate with acetic acid and test for *Chromium* by lead acetate.

(*b*) Dissolve in hydrochloric acid and test for *Iron*.

(*c*) Dissolve in hydrochloric acid, add potassium hydroxide in excess, boil, filter if necessary and add to filtrate excess of ammonium chloride—white transparent precipitate indicates *Aluminium*.

III. (b) To the filtrate from the iron group (which should have been filtered quickly as small quantities of $Zn(OH)_2$ and $Mn(OH)_2$ are liable to be precipitated along with the iron group), add ammonium sulphide, boil and filter: precipitate may contain ZnS (white), MnS (pink), NiS (black), CoS (black).

Note.—A blue filtrate from the iron group or a dark coloured one from the precipitate produced by ammonium sulphide, indicates the presence of Nickel, its sulphide being somewhat soluble in ammonium sulphide.

Add to precipitate cold dilute HCl, allowing to stand with occasional stirring, (a white precipitate of sulphur may separate out which may be neglected), filter.

Residue
Cobalt and *Nickel*
Dissolve in a porcelain basin with addition of a crystal or two of $KClO_3$, evaporate nearly to dryness, dilute, add KCN in excess, boil, add KHO and bromine-water in excess, boil, allow to stand and filter.

Precipitate
Nickel
Confirm.

Filtrate
Cobalt
Confirm.

Filtrate
Boil off H_2S, add a crystal of $KClO_3$ and boil again; cool, add KHO in excess and filter.

Residue
Manganese
Confirm (1) by fusing a portion of ppt. with solid $NaHCO_3$ and KNO_3 on a porcelain lid,—green mass if manganese is present. (2) dissolve ppt. in dil. HNO_3 and boil with red lead (Pb_3O_4)—purple solution.

Filtrate.
Zinc
Pass H_2S through filtrate to confirm,—white ppt. if zinc is present.

Separation of the Bases. Group IV.—Alkaline-Earths and Magnesium.

To the filtrate from Group III (*b*) add $(NH_4)_2CO_3$; this precipitates *Barium*, *Strontium* and *Calcium* but not *Magnesium*. Filter and wash the ppt. thoroughly.

Dissolve ppt. in $HC_2H_3O_2$ and add K_2CrO_4

Precipitate
Barium
Confirm by dissolving in dil. HCl and precipitating with dilute H_2SO_4.

Filtrate
Divide into two portions, (*a*) and (*b*).
To (*a*) add $CaSO_4$, heat to boiling and allow to stand for ten minutes—ppt. *Strontium*. Confirm by flame-test.
To (*b*) add Na_2SO_4 or H_2SO_4 to remove strontium (if any was found in (*a*)), filter this off and to filtrate add NH_4HO and $(NH_4)_2C_2O_4$—ppt. *Calcium*.

Filtrate
To *a small portion** of this filtrate add Na_2HPO_4—white ppt. indicates *Magnesuim*.
*(Preserve the remainder for examination under Gp. V.)

Group V. Potassium, Sodium, Ammonium.

(1) Test in O.S. for the presence of *Ammonium* salts.

(2) Evaporate filtrate from $(NH_4)_2CO_3$ precipitate and ignite in porcelain basin to drive off ammonium salts: dissolve residue in a little hot water and a little HCl and apply flame test—yellow, *Sodium*.
violet, *Potassium*.

If flame is yellow, view it through indigo prism or blue glass when it will appear red if *Potassium* is present.

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